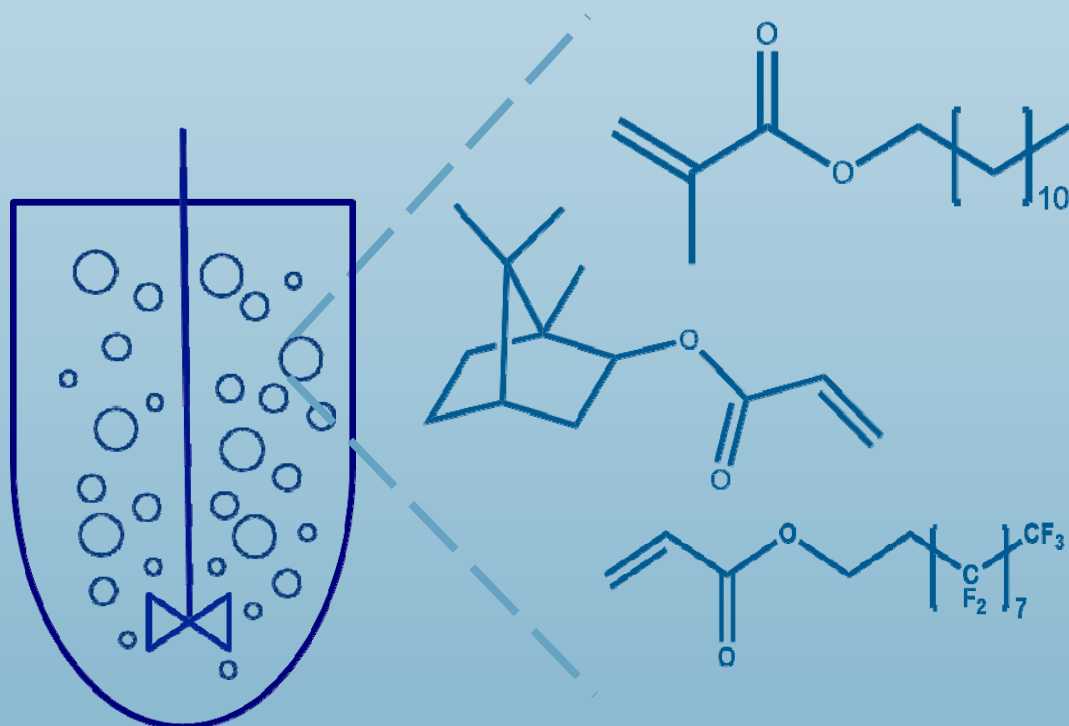


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EMULSION POLYMERIZATION OF SUPERHYDROPHOBIC MONOMERS





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(2017)

POLYMAT

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1.1. INTRODUCTION

It is difficult to overstate how essential water is to most of the living organisms of this planet, and humankind is no exception. However, while water and life are generally associated, the relation between water and most human-made materials and structures is not synergistic from an industrial point of view, ultimately leading to elevated operation and maintenance costs.^[1,2] Among the most notable victims are the construction and manufacturing industries, both of them producing materials ubiquitous to daily life in the 21st century. Taking this into account, it should come as no surprise that water resistance is one of the most important features of a protective coating, and finding ways to create coatings that can satisfy this and other performance properties expected from today's materials has been a prevalent subject of academic and industrial research since a few decades.^[3,4] Within this research, it is possible to identify two general ideas: i) the modification of the surface of an otherwise conventional coating in order to provide hierarchical roughness and severely decrease wetting;^[5-13] and ii) the use of materials with enhanced hydrophobicity, mainly during the synthesis of the binder that will eventually make up the final coating.^[3,11,14-19] Most contributions tend to follow the first approach when looking towards obtaining "superhydrophobic" surfaces; a term that has been coined for surfaces whose water contact angles are above

150°, and whose objective is to mimic structures found in nature such as the surfaces of lotus leaves or cicada wings.^[20] However, it is inherently difficult to implement this technology in a widespread range of products manufactured in large quantities due to the prohibitively expensive post-application surface modification. The second approach, i.e. employing more hydrophobic materials during the creation of the coatings themselves, has also proven to be quite challenging. From a long list of components that make up a typical coating, smaller molecules of hydrophilic nature such as surfactants, initiators and buffer salts, are kept to a minimum in order to maximize water resistance.^[21-24] Minor functional monomers such as n-isobutoxymethyl acrylamide^[25] or vinyltriethoxysilane,^[26] can also be used to meet similar ends through crosslinking, but in general, the increases on the hydrophobicity of the final coatings are not comparable to those of a surface modification. Taking into account that principal monomers make up the largest fraction of almost any binder, using monomers with enhanced hydrophobicity naturally results in coatings with improved water resistance. This effect can be verified within the hydrophobicity range of conventional water-borne monomers, by comparing the performance of a binder based on methyl acrylate, to similar binders based styrene and butyl acrylate, and observing an incremental improvement on the water resistance of the resulting films.^[24] By extrapolating

these results, it should be possible to, in theory, obtain coatings with outstanding water resistance by polymerizing monomers of extreme hydrophobicity. Industrially, the polymerization of said monomers has been carried out exclusively in solvent-borne media. However, due to growing environmental concerns and continually tighter governmental regulations,^[21] solvent-borne products have been replaced by water-borne alternatives, a trend that will continue in the years to come. Taking this information into consideration, finding an industrially cost-effective way to produce very hydrophobic polymeric dispersions in aqueous media has a tremendous potential yet to be exploited.

1.2. EMULSION POLYMERIZATION

Conventional emulsion polymerization is the most widely used process for the production of water-borne polymeric dispersions or emulsion polymers; as such materials are usually called when produced by this technique. The polymerization itself takes place through free-radical kinetics in a compartmentalized fashion within polymer particles. A typical formulation for this process would include monomers (50 – 55 wt%), deionized water (45

wt%), initiators (0.5 wt%), surfactants (0.5 – 3 wt%), crosslinking agents (0 – 0.5 wt%) and chain transfer agents (0 – 1 wt%).

The monomers are the basic building blocks of any polymer and are responsible for most of its final properties. They can be classified in major monomers, referring to those that make up the bulk of the final polymer, and minor monomers that generally contain a functional group and impart specific properties to both the polymer and the colloidal system. Major monomers are sub classified in hard monomers and soft monomers, based on the glass transition temperature of their respective homopolymers. Typical examples of hard monomers are styrene, methyl methacrylate and vinyl acetate. Likewise, butyl acrylate, 2-ethyl hexyl acrylate and VeoVa 10 belong to the soft monomer category. At least two monomers are used for the production of coatings in most practical cases, one of each sub category in order to control the glass transition temperature, minimum film formation temperature, hardness, tensile strength and other mechanical properties of the final polymer.

Initiators provide the free radicals that drive the polymerization, and are also divided in several categories. Thermal initiators gradually decompose and

produce radicals at relatively elevated temperatures, while redox initiators readily generate radicals as a result of a redox reaction and could be used at room temperature if needed. UV or other radiation-based alternatives do not enjoy widespread use in emulsion polymerization, although recently there have been some academic developments in the area.^[27,28] Initiators can also be classified as water or oil soluble initiators, depending on the media the radicals are being created. Thermal, water soluble initiators are the most common choice in emulsion polymerization. Redox initiator systems are used to a lesser degree during the bulk of the polymerization, although they are mostly implemented in post-polymerization steps.^[29,30]

Surfactants (also called emulsifiers) play a significant role during a typical emulsion polymerization. From a mechanistic point of view, early in the polymerization, they provide the micelles that serve as primary sites for particle nucleation. They also stabilize both monomer droplets and growing polymer particles, providing long-term stability to the final polymer dispersion as well. Surfactants can be ionic or non-ionic, depending on whether or not the hydrophilic group has an ionic charge or not. Ionic surfactants are further classified according to the nature of their charge in: i) anionic, when the hydrophilic group has a negative charge; ii) cationic, when the hydrophilic

group has a positive charge; and iii) zwitterionic, when both positive and negative charges can be present on the hydrophilic group, usually depending on process conditions. The use of each type of surfactant has its advantages and disadvantages, making surfactant selection a key variable in any polymerization.^[31] The electrostatic stabilization provided by ionic surfactants is excellent during the particle nucleation stage, facilitating the formation of relatively small polymer particles by maintaining high concentrations in the aqueous phase due low adsorption equilibrium constants and low rate of adsorption on the polymer/water interface,^[32] but their high sensitivity to electrolytes and poor freeze-thaw stability, among other disadvantages, is often problematic for their standalone industrial use. Non-ionic surfactants provide steric stabilization, insensitivity to electrolytes and resistance to freeze-thaw cycles, but are generally inefficient for particle nucleation.^[33] Due to this, mixtures of surfactants are quite common in industry and reaching an optimal value of the total quantity and ratio between surfactants is often an objective in emulsion polymerization.^[34]

Crosslinking and chain transfer agents are used to control both the fraction of crosslinked material of the polymer and its average molecular weight, respectively.^[35,36] When neither of these components is present, these

structural parameters are determined primarily by the polymerization temperature, initiator concentration, and by the monomer composition.^[37] Chain transfer agents (CTAs) are most commonly mercaptans, components containing one sulfur and hydrogen bond that is several orders of magnitude more susceptible to radical attack than the vinyl groups present in all monomers, and whose presence promotes the termination of existing polymer chains and simultaneous initiation of new polymer chains. Crosslinking agents, also known as crosslinkers, are multifunctional monomers capable of creating polymer networks through polymerization of their two or more vinyl groups. Examples of these components are allyl methacrylate and butanediol diacrylate, both capable of increasing the gel content during a polymerization to approximately 90% when used at concentrations as low as 0.23 mol%.^[38] Functional monomers, such as N-methylolacrylamide, diacetone acrylamide or acetoacetoxy ethyl methacrylate, can also initiate crosslinking reactions after the polymerization has concluded by simply removing water through drying or applying additional heat, often in the presence of another matching component.^[39]

Emulsion polymerization is a fairly well-known process, as evidenced by a large body of work spanning the last 70 years, and numerous reviews on the

subject.^[40-44] Commercial application of the technique usually takes place in stirred tank reactors, which can be employed in batch, semi-batch or continuous operation, this designation depending on whether or not material is fed and/or removed from the reactor during the polymerization. The colloidal and structural properties of the final product are generally affected by the type of process used, even for an identical set of ingredients, making this selection a critical parameter of the polymerization together with the degree of control, flexibility and safety of operation. Although based on these criteria semi-batch processes are the most adequate and indeed the most common in industrial settings, a batch process is typically used to illustrate the mechanism of emulsion polymerization in academia due to the sequential fashion at which the different individual steps occur. To this end, a general quantitative theory of emulsion polymerization in an ideal system, first introduced by Harkins,^[45-48] is still accepted today.

In a typical batch system, the totality of the monomers, surfactants, water and other ingredients used in relatively small quantities like CTAs, crosslinkers and buffers are present in the reactor since the beginning, with the exception of the initiator. The reactor is continuously stirred, allowing for the stabilization and dispersion of monomer droplets by the surfactants in the aqueous phase.

The excess surfactant not used to saturate the aqueous phase or to cover the surface of the monomer droplets, forms micelles instead; i.e. ordered clusters of surfactant molecules with the hydrophobic portion oriented towards the center while the hydrophilic portion is oriented towards the aqueous phase. Monomers, which are generally scarcely water soluble, diffuse to the hydrophobic nuclei of the micelles effectively swelling them.

The reactor is heated up to reach the reaction temperature (70 – 90°C), and a thermal water soluble initiator is added, marking the starting point of the polymerization. Radicals are formed in the aqueous phase, which are often too hydrophilic to enter directly into the organic phases, so they propagate instead by slowly adding the scarce monomer units solubilized in the aqueous phase until they become hydrophobic enough to enter the organic phases of the system. The newly grown radicals are referred to as “oligomeric radicals” or oligo-radicals in short. The number of monomer units an oligo-radical requires to become surface active depends on the hydrophobicity of both the initial radical and the monomer units added, where less hydrophobic radicals require the addition of more monomer units to become surface active, while adding units of hydrophobic monomers decreases this number in comparison to adding units of hydrophilic monomers.^[49]

There are two different paths leading to particle nucleation once a surface active oligo-radical is formed: i) entry of the oligo-radical into the monomer swollen micelles, where monomer units are quickly added eventually resulting in a polymer chain, a process known as heterogeneous nucleation;^[47] and ii) continued propagation of the oligo-radical in the aqueous phase until it becomes completely insoluble and precipitates, a process known as homogeneous nucleation.^[50] Entry of the oligo-radical into a monomer droplet could potentially take place, although to a relatively insignificant extent since the total surface area of the micelles is at least three orders of magnitude greater than that of the monomer droplets. Both nucleation mechanisms mentioned could be operative in any given system, although one usually predominates over the other based on the solubility of the monomers involved, where for monomers of relatively high water solubility, like methyl methacrylate or vinyl acetate, homogeneous nucleation predominates, while for monomers that are relatively water insoluble, like styrene or butyl acrylate, heterogeneous nucleation predominates.

A typical batch emulsion polymerization can be chronologically divided into three different intervals. During Interval I, monomer droplets, monomer swollen micelles and monomer swollen particles coexist in the reactor and

compete for the surface active radicals coming from the aqueous phase. When a radical enters a micelle, free-radical polymerization ensues and the micelle is now considered to be a polymer particle (heterogeneous nucleation). The monomer within the new particle is quickly consumed and replenished with fresh monomer that diffuses from the monomer droplets through the aqueous phase and into the polymer particle, resulting in a sudden increase of the size of the particle and consequently its surface area. The new surface area is stabilized with the excess of surfactant present in the reactor in the form of micelles. Simultaneously, a new polymer particle can also be formed through homogenous nucleation, resulting as well in diffusion of fresh monomer from the monomer droplets and surfactant previously forming micelles. Through both mechanisms, the number of micelles decreases while the number and size of the polymer particles increases, quickly becoming the main polymerization loci. This interval is the shortest, ending when there are no longer micelles in the reactor and particle nucleation ceases to occur, generally at conversions between 5 to 10%, depending on both the surfactant/monomer ratio and on the nature of said monomer(s).

During Interval II, only polymer particles and monomer droplets remain in the reactor. Polymerization takes place almost entirely within the polymer particles, and the monomer continues to be replaced with monomer from the monomer droplets. Consequently, the size of the polymer particles continues to increase while that of the monomer droplets decreases, eventually disappearing from the system at the end of Interval II. The diffusion rate of most conventional monomers in water is generally higher than the polymerization rate, and hence monomers partition between the phases of the system according to thermodynamic equilibrium, maintaining an approximately constant monomer concentration inside the particles. The transition between Interval II and Interval III generally takes place at conversions of 25 to 40%, depending on the extent at which the polymer particles can be swollen by the monomer(s). Most of the polymerization takes place at Interval III, when only polymer particles remain, and the monomer within them polymerizes. The monomer concentration gradually decreases, and consequently the polymerization rate, generally until all the monomer has been consumed.

As mentioned earlier, emulsion polymerization characterizes itself by having most of the polymerization taking place inside the relatively small polymer

particles. Within each particle, free-radical kinetics is quite similar to that of a bulk polymerization; however radicals are compartmentalized among all the particles in the system, making it unlikely that radicals from different particles will come into contact and terminate. Because of that, radicals in emulsion polymerization can accumulate in the polymerization loci and generally last longer than radicals in a bulk, solution or suspension polymerization system, allowing simultaneously for higher polymerization rates and higher molecular weights. Additionally, the latter two variables can be controlled independently through manipulation of the number of particles.

The different facets of emulsion polymerization previously exposed, together with the use an environmentally friendly continuous media (water), high flexibility of operation, wide variety of monomers available for (co)polymerization, and overall extensive degree of control of polymer and colloidal properties, make emulsion polymerization a desirable technique to use for many existing and new applications alike, at both academic and industrial scales.

1.3. WATER-BORNE POLYMERIZATION OF SUPERHYDROPHOBIC MONOMERS

The ability of monomers to transport themselves from the monomer droplets through the aqueous phase and into the growing polymer particles is essential in emulsion polymerization, a process that is widely acknowledged to take place by diffusion. While conventional monomers, like butyl acrylate or styrene, are not usually referred to as water soluble, they are however water soluble enough so that a thermodynamic equilibrium can be established between the phases of a typical emulsion polymerization, making the rate of polymerization the rate controlling step of the process. More hydrophobic alternatives, like 2-ethylhexyl acrylate or VeoVa 10, with water solubilities up to two orders of magnitude below that of styrene,^[51] have also been successfully copolymerized with other conventional monomers in emulsion polymerization, resulting in significant improvements on the performance of coatings aimed at the water barrier market.^[3] Polymerization of even more hydrophobic monomers has been found to be more challenging, encountering in the best cases issues with long induction periods associated to a heightened sensitivity to low concentrations of impurities,^[52] and in the worst cases low conversions and large fractions of coagulum.^[53] Because of that, conventional emulsion polymerization has been deemed ineffective for the

polymerization of monomers within this range of hydrophobicity, namely monomers with a water solubility lower than three orders of magnitude that of styrene, like dodecyl or octadecyl (meth)acrylate or 1,1,2,2-tetrahydroperfluorodecyl acrylate. These monomers will be referred to as “superhydrophobic” in this work, while the terms “hydrophobic” and “very hydrophobic” will be reserved to the ones like of styrene and VeoVa 10, respectively.

Several attempts have been made to overcome the transport limitations mentioned above, among which miniemulsification using high-energy methods^[40,54] like sonifiers, rotor-stators and high pressure homogenizers, or using low-energy methods^[55-61] such as temperature-induced phase inversion of a water in oil (w/o) emulsion, and the in situ formation of emulsifier at the oil-water interface,^[62-66] can be found. Other efforts have focused on improving the monomer transport through the aqueous phase by using additional components, such as macromolecular organic compounds having a hydrophobic cavity (e.g., cyclodextrins),^[67-72] or organic solvents to improve the solubility of these monomers in the continuous media.^[73,74] These alternatives to conventional emulsion polymerization will be revised in detail.

1.3.1. MINIEMULSION POLYMERIZATION

Miniemulsion polymerization refers to the free radical polymerization of submicron dispersions of monomer droplets, typically with average sizes between 50 and 500 nm that are colloidally stabilized against coalescence by a surfactant and diffusionally stabilized against Ostwald ripening using a costabilizer. Ostwald ripening refers to the degradation of the dispersion due to the diffusion of the components of the organic phase from small to large droplets, thermodynamically driven by the difference in their chemical potentials, more specifically by the difference given by the surface energy contribution. A costabilizer is a hydrophobic additive that essentially cannot diffuse through the continuous phase, whose function is to counteract the difference in the surface energy contribution to the chemical potential between small and large droplets by establishing an osmotic pressure difference in the opposite direction due its inability to diffuse between droplets. Hexadecane and cetyl alcohol are the costabilizers most often used in literature,^[75-80] although higher molecular weight materials, such as polymers, can also be used for the same purpose.^[81] These are usually referred to as hydrophobes because they lack the super-swelling capacity of lower molecular weight costabilizers.

1.3.1.1. MINIEMULSIFICATION BY HIGH-SHEAR DEVICES

Miniemulsions are usually formed by the breaking of the droplets of a coarse emulsion into much smaller droplets by the application of intensive shear forces and energy. This process, often called miniemulsification, can take place in a variety of equipment, the most commonly used being rotor-stator systems,^[82] sonifiers^[78] and high-pressure homogenizers.^[83,84] Unlike conventional emulsion polymerization, micelles are not present in the ideal system since the surfactant is fully utilized to stabilize the large surface area of the small droplets. Therefore, when radicals are formed in the system, they enter directly into the monomer droplets forming a polymer particle, making them the predominant particle nucleation loci. By means of droplet nucleation the need for diffusion through the aqueous phase of monomers and other water insoluble components is eliminated, allowing the incorporation of a wide variety of materials for multiple applications, among them superhydrophobic monomers.^[11,14-19] A few examples of these applications will be reviewed below:

Agirre et al.^[18] achieved the homo and copolymerization of stearyl acrylate (SA) with 2-ethylhexyl acrylate (2EHA) in semi-batch miniemulsion

polymerization, using Dowfax 2A-1 as emulsifier and ammonium persulfate as initiator, in order to produce semicrystalline, water-borne pressure sensitive adhesives. A sonifier was used to prepare the miniemulsions prior to their polymerization, and a costabilizer was not required due to the hydrophobic nature of the monomer mixtures. Unlike conventional semicrystalline polymers in which the backbone crystallizes, the long n-alkyl side chain of the superhydrophobic monomers (with chain lengths greater than 9 – 10 carbons) provided the crystallinity in this case. The conversion was monitored by reaction calorimetry, partly due to the extremely low volatility of the superhydrophobic monomer, reporting complete values after 3 hours.

Jansen et al.^[16] researched the reaction and monomer transfer characteristics of the miniemulsion polymerization of 4-tert-butyl styrene (TBS) and lauryl methacrylate (LMA). Sodium lauryl sulfate (SLS) was used as surfactant, hexadecane (HD) as costabilizer and either sodium persulfate or lauroyl peroxide were used as initiators. Sonication was used to prepare miniemulsions of both monomers separately, and to prepare miniemulsions of mixtures of both monomers. The miniemulsions of the separate monomers were blended and then polymerized, and the results were compared to those found for the polymerization of the miniemulsions of the previously prepared

monomers mixtures. The authors observed similar thermal transitions by DSC in both polymers, suggesting mass transfer between individual droplets had taken place prior to polymerization. When interactions between droplets were physically hindered through the use of a membrane, mass transfer between the droplets of the most hydrophobic monomer studied, LMA, was negligible; while for TBS and conventional monomers like methyl methacrylate and butyl acrylate, a copolymer was obtained, suggesting that diffusion through the aqueous phase (and the membrane) was the operating transport mechanism in that case. They concluded that mass transfer by collisions made up a major contribution to overall monomer transport in the miniemulsion polymerization of TBS and LMA.

1.3.1.2 MINIEMULSIFICATION BY PHASE INVERSION

There are two types of phase inversion processes currently applied in industry and academia, transitional phase inversion and catastrophic phase inversion, both of which have received much attention as a consequence of the numerous applications in the food,^[85] pharmaceutical,^[86] cosmetics,^[87,88] and petroleum industries.^[89,90] More recently, these methods have been claimed to be low-energy alternatives to the formation of stable

mini-emulsions, capable of polymerization through droplet nucleation.^[55-58,60,61,91]

Despite enjoying widespread academic and commercial interest, the underlying mechanisms of phase inversion are still under debate. That is particularly evident for catastrophic phase inversion, whose mechanism involving multiple-emulsion occurrence has been identified as one of the main sources of complexity.^[92] Nonetheless, several approaches have been proposed to generalize and facilitate new implementations of phase inversion theory that are still applicable; among them, the hydrophilic-lipophilic deviation parameter and bidimensional formulation-composition maps are worth revising.

The hydrophilic-lipophilic deviation (HLD) is a dimensionless parameter introduced by Salager et al.^[93] that characterizes the affinity of the surfactant towards each of the phases in a specific surfactant-oil-water mixture. The parameter accounts for the combined effect of the so-called formulation variables, according to Salager et al.^[94] classification. It can be calculated using the following equations for systems stabilized with ionic (Equation I - 1) or non-ionic (Equation I - 2) surfactants:

$$HLD = \sigma + \ln S - k * ACN - t(T - 25) + a * A \quad (\text{Equation I - 1})$$

$$HLD = \alpha - EON + b * S - k * ACN - t(T - 25) + a * A \quad (\text{Equation I - 2})$$

where ACN is the alkane carbon number or its equivalent ($EACN$) in case the oil phase is not an alkane; α , k , σ , and t are surfactant parameters that vary according to structural features such as the length and degree of branching hydrophobic tail; EON is the number of ethylene oxide groups in the surfactant, b and a are constants characteristic of each type of salt and alcohol, S and A are the salt and alcohol concentration, and T is the temperature in °C.

In emulsions with $HLD < 0$, the surfactant has more affinity for the aqueous phase, and tends to form micelles that stabilize oil-in-water (o/w) emulsions. The opposite applies to emulsions with $HLD > 0$, while $HLD = 0$ corresponds to the so-called “optimal formulation”, a point at which the affinity of the surfactant towards both aqueous and oil phases is equivalent and a bicontinuous microemulsion phase can be formed.

The HLD parameter is particularly useful when working with bidimensional formulation-composition maps.^[95-97] In such maps, HLD runs on the vertical

axis while either the oil-to-water ratio or another related composition variable runs on the horizontal axis, as shown in Figure I - 1.^[96] The map is divided into six sections by a so-called inversion line in the form of a step, with each section representing an emulsion having either an oil rich continuous phase (B), a water rich continuous phase (C) or evenly distributed oil and water phases (A), and being stabilized by a surfactant with a higher affinity either towards the oil phase (+) or towards the water phase (-).

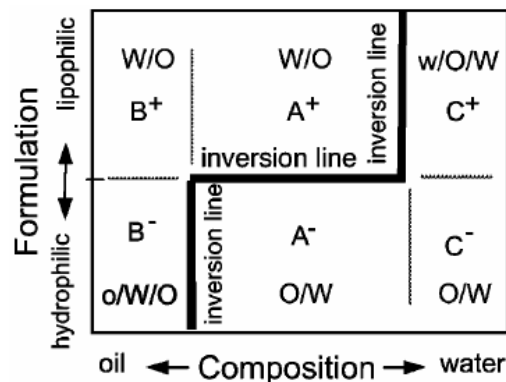


Figure I - 1. Bidimensional formulation-composition map^[96]

These emulsions types can be characterized as either normal or abnormal according to whether or not they follow the Bancroft's rule, i.e. the phase for which a surfactant has the most affinity will be the continuous phase. Normal emulsions are those that follow the Bancroft's rule, while abnormal emulsions do not. In Figure I - 1, A+, A-, B+ and C- are kinetically stable normal emulsions, since there is no evident conflict between the affinity of the

surfactant and which phase makes up a large majority of the emulsion. On the other hand, emulsions B⁻ and C⁺ are classified as abnormal because there is indeed a conflict between formulation and composition variables that is often resolved by multiple emulsion formation.^[98-100] For example, in the case of an emulsion type B⁻, the surfactant has a strong affinity towards the water phase so an internal emulsion where water is the continuous phase is stabilized within the larger oil phase, resulting in an o/w/o emulsion.

A classification of surfactant-oil-water systems containing microemulsion phases, that is particularly useful in phase inversion research, was proposed by Winsor in 1948, and is presented in Figure I - 2.^[101] Within this scheme, when the surfactants used are mostly soluble in water, an o/w microemulsion is formed that is in equilibrium with an excess oil phase, in what is regarded as a type I system. In the opposite case, when the surfactant is mostly oil soluble, a w/o microemulsion that coexists with an excess water phase is formed instead, in a type II system. When the affinity of the surfactant for the oil and water phases is similar, a surfactant-rich middle phase microemulsion that is in equilibrium with excess water and oil phases is obtained, in a type III system. Furthermore, should relatively large quantities of surfactant be

available, a single phase system consisting only of a middle phase microemulsion would be formed, in what is known as a type IV system.

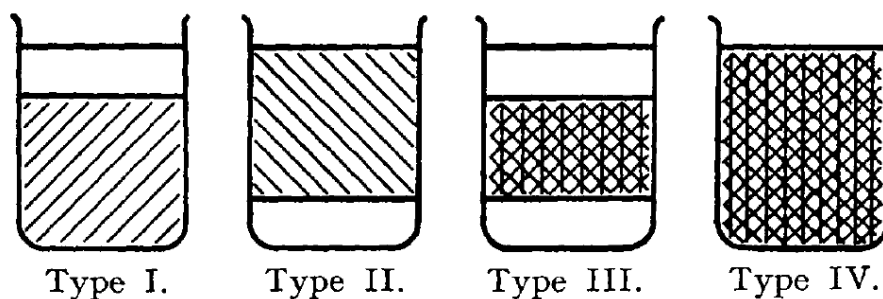


Figure I - 2. Classification of microemulsions according to Winsor^[101]

In a formulation-composition map, transitional phase inversion is represented by a vertical displacement, i.e. a single or multiple formulation variables are changed until the point at which the affinity of the surfactant towards both aqueous and oil phases is equivalent, at $HLD = 0$. At this point, a bicontinuous microemulsion phase is formed, resulting in what could be regarded as a Winsor type III system, or if enough surfactant is available, a Winsor type IV system. By modifying the HLD of the emulsion back to its original value, the bicontinuous microemulsion phase disintegrates when leaving the optimal formulation range, yielding very small droplets.

Generally speaking, any formulation variable or combination of them (salinity, nature of emulsifiers, nature and amount of alcohol costabilizer,

hydrophobicity of the oil phase) can be varied in order to bring the emulsion to this “optimal formulation” point. However, temperature is the variable most commonly used and this process is usually referred to as Phase Inversion Temperature (PIT) method. In this particular case, polyethoxylated non-ionic emulsifiers, which owe their thermo-sensitivity to the reduction in the hydration number of ethylene oxide groups at elevated temperatures,^[102] are the most commonly used. This method was originally introduced by Shinoda and coworkers,^[103] and the mechanistic steps involved have been recently summarized by Friberg et al.^[104]

Catastrophic phase inversion is triggered through the addition of the internal phase of an emulsion until the closed packing value of said emulsion is reached. At this point, the internal phase droplets are easily elongated under continuous stirring until they merge into a single bicontinuous phase that eventually decomposes into fine droplets.^[92,105] Unlike transitional phase inversion that takes place between two normal emulsions according to Bancroft’s rule, catastrophic phase inversion occurs from abnormal to normal emulsions, i.e. either from B⁻ to A⁻ or from C⁺ to A⁺ in the formulation-composition map (Figure I - 1). The lack of reversibility, as well as high susceptibility to procedural variables such as addition rates and vessel

geometries,^[95-100,106-108] in catastrophic phase inversion are generally associated to this fundamental mechanistic difference in comparison to transitional phase inversion.

1.3.1.3 POLYMERIZATION OF PHASE-INVERTED MINIEMULSIONS

A few examples pertaining to polymerization of emulsions prepared through phase inversion can be found in literature,^[55-61] and are reviewed below.

Spernath and Magdassi^[55] used the PIT method to produce a polymerizable miniemulsion of lauryl acrylate, using polyethoxylated non-ionic emulsifiers, Brij 96V (oleyl alcohol with 20 mol ethylene oxide units), and combinations of Brij 96V and Brij 92V (oleyl alcohol with 2 mol ethylene oxide units). The emulsions contained 20 wt% oil phase (lauryl acrylate, with or without a crosslinker) and 4 – 7 wt% emulsifier. An aqueous solution of NaCl (10 mM) was used as the continuous phase. The coarse o/w emulsions were heated above the temperature at which inversion to w/o emulsions occurred and then rapidly cooled in an ice bath, resulting in o/w miniemulsions. The PIT was previously determined by measuring the conductivity of the emulsions during the heating process. The nano-droplets were polymerized, yielding

nanoparticles having an average diameter between 50-120 nm with a narrow size distribution, using a water-soluble thermal initiator (ammonium persulfate) and activated by ferrous ions, Fe^{+2} . Styrene was added to the system to form hydrophobic radicals that could enter the droplets once the polymerization stage began. A reduction of the droplet size from approximately 1000 nm to 200 nm was observed at 72 °C before and after phase inversion, followed by a reduction to 50-120 nm after polymerization.

Alvarado and coworkers^[58] also implemented the PIT method to prepare miniemulsions of hexyl methacrylate stabilized with Brij 56 (oleyl alcohol with 10 mol EO), and squalene as costabilizer. Surfactant and costabilizers concentrations were between 11-15 wt% and 5 wt%, respectively, with a solids content of up to 20 wt%. The conditions were selected in order to obtain a single phase microemulsion (Winsor IV) at the inversion temperature range of 56 – 61 °C. The addition of the costabilizer was necessary to preserve the colloidal stability of the miniemulsions against Ostwald ripening, whose droplet sizes were as low as 32 nm for the highest surfactant concentrations. Polymerization of the miniemulsions were performed at 20°C using small amounts of the redox pair potassium persulfate and ferrous

sulfate, with the authors claiming complete conversions in less than 5 minutes and evidence of droplet nucleation as the predominant mechanism.

Suzuki et al.^[60] reported the preparation by PIT and later polymerization of styrene miniemulsions in the presence of pyrene at contents from 0 to 10 wt% based on monomer. A poly(ethylene oxide) nonyl phenyl ether with an average of 20 EO was used as surfactant at a weight ratio of 1:1 with respect to the monomer, and with solids contents below 10%. A phase inversion temperature of 53 °C was determined by monitoring the electrical conductivity and transparency of the emulsion. The polymerizations were carried out at the phase inversion temperature using potassium persulfate as initiator. Fluorescence spectroscopy was utilized to quantitatively determine the amount of pyrene present in the polymer particles. It was claimed that polystyrene nanoparticles containing elevated amounts of pyrene with an average diameter as low as 22 nm were achieved,

Sasaki et al.^[61] carried out the miniemulsification of styrene by PIT, using amphiphilic comb-like block polymers synthesized by ATRP of styrene and oligo(ethylene glycol) methyl ether methacrylate, as surfactants. These polymeric surfactants were used at a 1:2 weight ratio with the monomer, and

were found to be good costabilizers as consequence of the hydrophobic polystyrene chains dissolving in the oil phase. The phase inversion temperature was approximately 90 °C, while the polymerizations took place at 40 and 60 °C, using water and oil-soluble thermal initiators in tandem. Latexes with average particles sizes between 30 and 120 nm were synthesized by controlling the styrene chain length of the surfactant, with total solids contents close to 10 wt%.

Galindo-Alvarez et al.^[56] implemented the alternative Near-PIT method, where the initial monomer emulsion is heated to a temperature a few degrees lower than the PIT, in order to prepare styrene miniemulsions using combinations of alkyl polyglycoethers Brij 78 (stearyl alcohol with 20 mol ethylene oxide units) and Brij 700 (stearyl alcohol with 100 mol ethylene oxide units) as surfactants, and 5 wt% of hexadecane as costabilizer. Miniemulsions with inversion temperatures above 80 °C, were polymerized during 24h at 50 °C, with potassium persulfate as initiator and at contents of 20 wt% of monomer and 5.2 wt% of surfactants, yielding polymer dispersions with lower particle sizes than miniemulsions prepared by both traditional PIT and through the use of energy-intensive equipment. The principle behind this PIT variant is that not only interfacial tension reaches a minimum at the optimal formulation point,

but also the colloidal stability of the emulsion as a consequence of the trapping of surfactant in the microemulsion phase.^[109,110] The authors argued that, as far as the emulsion droplet size is concerned, a decrease on interfacial tension enhanced the efficiency of the mixing process thus improving droplet breakup, while on the other hand, the decrease on colloidal stability that the system experienced at $HLD = 0$ enhanced droplet coalescence, resulting in larger droplets. The result of these conflicting trends is that the minimum droplet size was not found at $HLD = 0$, but rather at a few degrees from it, where coalescence events were not as significant. This technique can be traced back to the pioneering work of Shinoda et al.^[111]

Sadtler and coworkers^[57] employed catastrophic phase inversion to prepare styrene miniemulsions. Brij 98, a polyethoxylated non-ionic emulsifier (stearyl ether with 20 ethylene oxide units) was used. Hexadecane was used as costabilizers and potassium persulfate as initiator. An aqueous solution of NaCl (10 mM) was added with a dosing pump to the continually stirred organic phase (STY:HD ratio of 95:5) at 50 °C. The authors found that in order to prepare a stable and polymerizable miniemulsion, the aqueous phase had to be added until a two phase region comprising a o/w microemulsion phase and free monomer was present (Winsor III). Following

the low-energy miniemulsification process, a potassium persulfate solution was added to start the polymerization for a total of 24 hours. Particle sizes determined by DLS oscillated between 36 and 50 nm, depending on the monomer-to-emulsifier ratio and addition rate of the aqueous phase. The authors claimed this contribution as the first polymerizable system to be prepared using exclusively catastrophic phase inversion.

Campbell et al.^[59] implemented catastrophic phase inversion to prepare an intermediate emulsion before using high-energy homogenization with a rotor-stator system. The organic phase was comprised of methyl methacrylate and stearyl acrylate (7 wt% based on MMA). An anionic surfactant, sodium dodecyl benzene sulfonate, was used at a concentration of 3 wt% based on monomer. The target organic phase content was between 60 and 80 wt% after the miniemulsification process, which was eventually diluted to 40 wt% before polymerization. The aqueous phase was added to the organic phase under mild stirring until a significant increase in conductivity was detected, suggesting the occurrence of a phase inversion event. High-energy miniemulsification with a rotor-stator system at 3000 rpm took place in order to obtain the final stable miniemulsions, which were polymerized at 70 °C with the addition of potassium persulfate. The authors concluded that by using

catastrophic phase inversions, high-energy homogenization times could be reduced up to 4 times, for higher monomer content miniemulsions that could later be diluted to the desired values.

1.3.2. CYCLODEXTRINS AS TRANSPORT CATALYSTS

This method was developed by Lau et al.^[67] and it has been explored by several other authors.^[69-72,112,113] The basis of this approach relies on the solubilization of the superhydrophobic monomers through complexation with a macromolecular organic compound having a hydrophobic cavity, the most common example of one being a cyclodextrin (CD). The newly formed complex is water soluble and able to readily diffuse from the monomer droplets, through the aqueous phase and to the polymer particles, overcoming in that way the transport limitations that hinder conventional emulsion polymerization of said monomers. The process is said to require relative small amounts of CD, reportedly fewer than 2 wt% based on monomers in some cases, and the formation of the water soluble complex to be reversible, allowing the CD to be free to participate in repeated transport cycles. Because of this dynamic behavior, cyclodextrins are usually referred to as “phase transport catalysts” when used in emulsion polymerization. A

theoretical model explaining this mechanism has been published.^[68] Monomers such as lauryl (meth)acrylate and stearyl (meth)acrylate have been co-polymerized in conventional emulsion polymerization conditions using this method, where the cyclodextrin of choice has been methyl- β -cyclodextrin.^[69-71,112,113] Multiple performance evaluation papers and patents have been published regarding the benefits of incorporating different amounts of hydrophobic components through the use of phase transport catalysts. Among the properties usually benefited with this technique are absorption of oil and grease, as well as improved water and water vapor resistance.^[72]

Leyrer et al.^[71] achieved the homopolymerization of stearyl acrylate (SA), and its copolymerization with styrene and/or butyl acrylate using methyl- β -cyclodextrin. The homopolymerization of SA was performed in batch emulsion polymerization at 20% solids content, using sodium dodecyl benzene sulfate as surfactant and sodium persulfate as initiator. The copolymerizations took place in semi-batch over a period of 4 hours, up to a final solids content of 43%, with a variable amount of SA from 10 to 40 wt% based on monomers. The content of CD was adjusted in the range of 12.5 to 20 wt% based on monomers, from the lowest to the highest SA containing polymerizations. They observed a reduction in the particle size together with an increase in the

molecular weight as the composition of SA increased. They also found that adding CD increased the average particle size in most cases, which they attributed to a part of the surfactant molecule that could have been complexed by the cyclodextrin, thus reducing the number of surfactant micelles.

The semi-batch emulsion polymerization of lauryl and stearyl methacrylate, using β -cyclodextrin as transport catalyst was investigated by Rimmer and coworkers.^[70] Dowfax 2A1 was used as surfactant and potassium persulfate as initiator. The theoretical solids content was 22%, while the cyclodextrin content was changed from 0 to 11 wt% based on monomers. Polymerizations in absence of cyclodextrin lead to coagulum contents over 50%, however when contents above 5 wt% based on monomers were utilized conversions above 95% and coagulum contents under 3% were obtained. Polymerizations in absence of surfactant lead to high coagulum contents, suggesting that CD does not significantly affect colloidal stability but rather promote monomer transport and polymerization in particles whose size are within the submicron range.

1.3.3. **EMULSIFIER COMBINATION IN EMULSION POLYMERIZATION**

Several researchers have found varying degrees of success in the polymerization of superhydrophobic monomers by carefully optimizing basic parameters of an emulsion polymerization recipe, such as the emulsifier(s) and initiator nature and concentrations, or the polymerization procedure itself, that are relevant within the framework of this thesis.

Tauer and coworkers^[53] studied the batch polymerization of several monomers of varying water solubility, including TBS and LMA, using different combinations of potassium persulfate and symmetrical poly(ethylene glycol) (PEGA) azo-initiators, with sodium lauryl sulfate (SLS) and disodium-N-stearoyl-L-glutamate (DSNSG) as emulsifiers. The monomer content for all the polymerizations was 20% in weight, while the emulsifier content was either null (i.e. emulsifier free) or 1 wt% based on monomer. The authors found that, on emulsifier free polymerizations, the increase of stirring speed from 300 to 1200 rpm led to a higher polymerization rate and final conversion, attributed to an increase in the diffusion rate of the more hydrophobic monomers through the aqueous phase, and the formation of smaller droplets which would favor a more compartmentalized system for more hydrophobic

monomers. Additionally, a significant effect in the particular combination of monomer/stabilizer/initiator was observed for the emulsifier-containing polymerizations, where the use of the more hydrophobic PEGA initiators together with the more hydrophobic emulsifier, DSNSG, resulted in the highest conversion and colloidal stability for the polymerization of LMA. The results indicated that both, the kind of initiating radical as well as the nature of the stabilizers, have astonishing effects on the polymerization of superhydrophobic monomers. A possible stabilizing steric effect provided by the longer PEG chains of the macro azo-initiator on the polymer surfaces, or an effect of said PEG chains on the partition coefficient of LMA molecules between the monomer droplets and the aqueous phase are suggested as possible driving forces of the success of this polymerization.

Avramidis and Bassett^[114] presented a method for the emulsion polymerization of very hydrophobic monomers, using as examples the homo and co-polymerizations of VeoVa 9 and VeoVa 10, with tert-butyl hydroperoxide (TBH) and sodium formaldehyde sulfoxylate (SFS) as oxidant and reductant in a redox system, respectively. The method was based on the combination of surfactant of different critical micelle concentration (CMC) during the course of a semi-batch polymerization. According to the authors,

the surfactant employed is selected on the basis that its solubility, as reflected by the CMC, is similar to the solubility of the monomer or monomer mixture that is to be polymerized. Accordingly, any combination of low-CMC surfactant and hydrophobic monomer can be used as long as the solubility of both in the polymerizing medium is similar. In other words, it is preferred that the more hydrophobic the monomer the more hydrophobic, and hence the lower the CMC, of the surfactant to be used in the polymerization. In the examples presented, low CMC surfactants are initially dissolved in the monomer mixture while a smaller portion of a high CMC surfactant is dissolved in water. The monomer mixture is fed to the aqueous phase together with aqueous solutions of TBH with a relatively high amount of a third surfactant of moderate CMC, and SFS. The total amount of emulsifier varies around 2 wt% based on monomer. The latexes produced have solids contents around 50% and average particle size in the range of 200 to 600 nm.

Back and Schork^[17] studied the batch polymerization of isobornyl acrylate (IBA) under conventional emulsion polymerization conditions. Both, potassium persulfate and TBH/SFS/FeSO₄, were used independently as initiators and SLS at multiple concentrations was used as emulsifier. The solids content for all the polymerization was approximately 25 wt%. They

found that emulsion polymerization of this monomer is feasible, although it was possibly diffusionally limited given its low water solubility. A high sensitivity of the particle number and polymerization rate to surfactant level was observed. This effect is less pronounced at high surfactant concentrations while using potassium persulfate, because of the surface active nature of the ionic chain ends derived from this initiator. They also observed a delay in the conversion vs. time curves caused by slow nucleation which they attributed to slow growth of oligomers generated from the water-soluble initiator, to trace amounts of inhibitor in the monomers, and to a heightened sensitivity of these effects when polymerizing monomers with very low water solubility, as reported previously for VeoVa 10.^[52] Special attention was given to the unexpectedly high conversion values obtained from the polymerizations at emulsifier concentration below the CMC with TBH as initiator; conditions at which submicron particles are not likely to be created for a very hydrophobic monomer allegedly incapable of undergoing homogenous nucleation. The authors proposed two hypotheses for the nucleation of submicron particles: i) the solubilization of oligomers with surfactant molecules in the aqueous phase followed by coagulation of these precursor particles to form polymer particles; and ii) solubilized oligomers adsorb onto the monomer droplets that under the shear of agitation produce

small droplets that would be protected from Ostwald ripening long enough to initiate polymerization. In both cases, a collision-based mechanism would be responsible for the monomer transport throughout the polymerization.

1.3.4. OTHER METHODS

A few other approaches through which superhydrophobic monomers have been polymerized can be found in the open literature, although unlike the contributions described in the previous subsection, they require the incorporation of components and/or conditions atypical for emulsion polymerization that have not been previously covered in this text.

Organic solvents, such as ethanol^[115] or propylene glycol^[73] have been used to improve the solubility of superhydrophobic monomers in the continuous phase, promoting monomer transport by diffusion between droplets and particles. Ahmad and coworkers^[115] studied the solvent effect of ethanol on the batch copolymerization of LMA and MMA, using potassium persulfate as initiator and poly(vinyl pyrrolidone) or poly(vinyl alcohol) as surfactants. The content of ethanol on the continuous phase was changed from 10 to 40 wt%, observing nearly complete conversions for concentrations above 30%. The

system was considered to act as both, a dispersion polymerization with respect to the MMA, and as an emulsion polymerization with respect to LMA.

Another method proposed was the *in situ* formation of emulsifiers as a low-energy alternative to produce stable miniemulsions and circumvent monomer transfer through the aqueous phase. This method has been proposed to either reduce the miniemulsification time on high energy processes,^[63,65] or to eliminate it completely.^[62,64,66] It is based on the neutralization of an oil-soluble carboxylic acid with an alkaline aqueous solution, resulting in lower interfacial tension than the equivalent pre-synthesized emulsifier. This is presumably a consequence of the surfactant forming directly and at a high rate at any newly generated interface rather than having to diffuse from the aqueous phase to the interface, thus reducing the rate of droplet degradation. Guo and coworkers^[66] have conducted several studies on the effect of the length of the carboxylic acids and the nature of the counter-ions of the water-soluble alkalis used in the synthesis of the *in situ* emulsifiers, concluding that the combination of oleic acid and potassium hydroxide provided optimal results, and at given conditions a droplet nucleation mechanism was favored over conventional emulsion polymerization. El Jaby et al.^[63,65] implemented this technique in tandem with high energy homogenization, resulting in a

significant reduction of total homogenization time and energy consumption. Stability at higher solids content (approximately 40%) was also achieved on the latter study. At the time of writing, there have been no applications towards the polymerization of superhydrophobic monomers based on this technique, where styrene has been the common monomer of choice.

Recently, Zhang and coworkers^[116] have been able to polymerize superhydrophobic monomers in emulsion polymerization by conducting the polymerization at elevated temperatures (100 – 150 °C) and pressures (1 – 10 bar) in order to increase the saturation concentration of the monomers and their diffusivity in water. They presented examples of the copolymerization of superhydrophobic monomers like Visiomer®C13-MA, Visiomer®C17.4-MA, LMA, SMA and 1,1,2,2-tetrahydroperfluorooctyl acrylate, with conventional monomers. Solids contents were around 37 wt%, with contents of superhydrophobic monomers oscillating between 20 and 47 wt% based on monomers. Water absorption tests showed promising results when compared to reference conventional emulsion polymers.

1.3.5. CHALLENGES AT AN INDUSTRIAL SCALE

It is within the scope of this thesis to develop a method through which high levels of superhydrophobic monomers can be incorporated in water-borne polymeric dispersions, for both academic and industrial purposes alike. Water-borne polymeric dispersions of superhydrophobic monomers can be catalogued as high performance materials, particularly towards applications involving excellent water-barrier properties. On top of that they need to satisfy the usual requirements the market has come to expect from conventional emulsion polymers, such as, high solids contents, low amount of volatile organic compounds (VOC) and residual monomers, adequate film formation and film appearance, long shelf-life and colloidal stability, rheology control and excellent mechanical properties, just to name a few. To be successful, these materials also need to be able to be produced in a flexible, reproducible and cost-effective way at an industrial scale, under safe and environmentally friendly conditions. Due to these multiple constraints, some of the alternatives to conventional emulsion polymerization discussed above, while technically feasible, present challenges that cannot be reconciled with the current expectations.

The industrial challenges of implementing miniemulsions polymerization have been recently reviewed by Asua.^[17] Despite being a technique used extensively in laboratory scale during the last 40 years, the special equipment required for miniemulsification have met heavy resistance at an industrial scale. Sonifiers, while very effective to produce small droplets, only do so in a limited area near the sonication tip, which limits its use to small vessels containing emulsions with low viscosities. High pressure homogenizers and rotor-stator systems are more suitable for large scale miniemulsification; however they are regarded as energy-intensive equipment whose use should be minimized. Static mixers are very attractive due their relatively low energy consumption; however multiple passes of the emulsion through the mixer in a loop arrangement are required, resulting in significant time investments.

Miniemulsification by either phase inversion method has its set of drawbacks. Transitional phase inversion, regardless of the variable adjusted to induce a change on the interfacial curvature, requires elevated concentrations of surfactant. On the other hand, the surfactant demand for a typical catastrophic phase inversion experiment is usually lower than for its transitional counterpart; however the droplet sizes obtained are usually in the micron range, suggesting it would require some degree of optimization before

either of these techniques can be used to develop a competitive emulsion polymer.

The use of cyclodextrins provides an effective and proven way of incorporating superhydrophobic monomers to otherwise conventional latexes; however both cyclodextrins and their derivatives are expensive compared to other components used in emulsion polymerization, and their presence in the final polymer dispersion (and hence on the final coating) detract from the expected hydrophobic character. In addition, materials made up mostly of very hydrophobic and superhydrophobic monomers require prohibitive amounts of cyclodextrins in order to be polymerized.

Through emulsifier combination in emulsion polymerization it has been possible to polymerize very hydrophobic monomers at conditions similar to those used in conventional emulsion polymerization. However, the limited number of examples involving superhydrophobic monomers, as well the limited conditions at which these polymerizations were possible, suggest that significant efforts would be required in order to develop a method and understand its underlying mechanism.

Organic solvents are classified as VOCs, and their presence should be avoided as much as possible due to environmental and labeling concerns. Because of this, implementing them at the synthesis stage would require successive downstream purification stages, which are not commonly available. It is worth mentioning that the amount of solvent required to obtain a significant extent of polymerization of superhydrophobic monomer is very high (40 wt%), even in the presence of hydrophilic monomers in the mixture.

The low solids content attainable for polymerizations with *in situ* generated surfactants (about 10 wt%) without high energy homogenization makes it undesirable in an industrial setting. On the other hand, its use in combination with high energy miniemulsification could be of benefit in cases where the application of such processes is economically justified; however the excess of alkali in the recipes could potentially become a problem in the final properties of the polymers produced.

Polymerization at high temperature and pressure also presents its set of challenges, both in terms of implementation and associated operation costs. Additionally, despite the claims of the authors, the examples presented only

involve incorporation of moderate amounts of superhydrophobic monomers at solids contents fewer than 40 wt%.

In summary, most of the different techniques evaluated make a valid case towards the development of a general method for the polymerization of superhydrophobic monomers, but they have drawbacks that need to be carefully addressed and considered before selecting the ones that show the most promise for future development. To that end, the requirement of high energy homogenization devices, extensive downstream purification steps and operation at high pressures and temperatures, are outside of established industrial practices and hence beyond the scope of this thesis. The high demand of hydrophilic additives to synthesize a polymer containing mostly superhydrophobic monomers make the use of cyclodextrins as transport catalysts undesirable. The low solid contents together with the requirements for high amounts of hydrophilic species also disqualifies the generation of *in situ* surfactants in absence of high energy homogenization.

Emulsifier combination in emulsion polymerization remains as the most promising option, although it requires the largest development towards reaching a clear understanding. Additionally, while miniemulsification by

phase inversion requires relatively high amounts of emulsifiers, unlike the hydrophilic species involved in other low-energy emulsification techniques, most of this emulsifier remains available in the final dispersion to either stabilize additional polymer surface area when used as a seed, or to act as an additive in blends as will be shown in the present study.

1.4. OBJECTIVE

The main objective of this thesis was to develop a general methodology to polymerize superhydrophobic monomers through emulsion polymerization, avoiding the use of solvents and high-energy miniemulsification steps. In order to reach this goal, a technique called emulsifier combination in emulsion polymerization was developed, requiring the identification and study of the most significant variables of successful semi-batch emulsion polymerizations of different combinations of superhydrophobic monomers and emulsifiers. Simultaneously, miniemulsification of superhydrophobic monomers by phase inversion was implemented, involving the determination of effective emulsifier mixtures and the optimal ratios between emulsifier and superhydrophobic monomer content. Finally, the performance of the polymer dispersions obtained in this work was evaluated as standalone latexes and in commercial

coatings formulations, resulting in significant improvements in the water-barrier properties of the reference polymers.

1.5. OUTLINE OF THE THESIS

This thesis has been organized in five chapters that deal with the following subjects:

In Chapter II, emulsifier combination in emulsion polymerization is developed and evaluated as a technique to polymerize superhydrophobic monomers. The process variables governing the polymerization of these monomers in batch and semi-batch strategies are identified and a polymerization mechanism is proposed.

Chapter III covers the implementation of miniemulsification through phase inversion in the polymerization of superhydrophobic monomers. A selection of suitable surfactants, determination of phase inversion temperature points and optimization of total monomer and surfactant contents is described.

An evaluation of the performance of several latexes containing high amounts of superhydrophobic monomers synthesized by different techniques, both as pure binders and as fully formulated water-borne coatings, is presented in Chapter IV.

In Chapter V, the most relevant conclusions of this thesis are presented.

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Chapter II. EMULSIFIER COMBINATION IN EMULSION POLYMERIZATION

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2.1. INTRODUCTION

As reviewed in Chapter I, polymerization of superhydrophobic monomers is a challenging, yet commercially desirable objective that has not been quite reached in industrial aqueous media polymerization, mostly due to the scarce water solubility of the compounds involved. While several alternatives have been proposed, none of them have been able to satisfy all the criteria required for it to be successful in an industrial environment, such as employing a reduced amount of hydrophilic species, being able to be applied with conventional equipment, having a large degree of flexibility in terms of reactants and polymerization strategies, using relatively inexpensive materials, and creating a final product with a performance that is significantly above that of conventional polymers. In this chapter, emulsifier combination in emulsion polymerization (EC) will be introduced as a potential candidate to satisfy the criteria mentioned above. This technique is loosely based on the use of at least one emulsifier with low critical micelle concentration to enable the efficient polymerization of hydrophobic monomers mentioned in Chapter I.

Avramidis et al.^[1] addressed the polymerization of VeoVa monomers, using them as a model for very hydrophobic monomers. The use of at least one

very low CMC emulsifier was attributed to be the determining factor of the success of these experiments, and it was claimed that it would work for other hydrophobic monomers in general although no examples outside VeoVa monomers were presented. It was also mentioned that at least one emulsifier should be selected on the basis that its solubility, as reflected by the CMC, was similar to the solubility of the monomer(s) meant to be polymerized. A similar conclusion was reached by Tauer et al.^[2], whom through the use of a hydrophobic surfactant, disodium stearyl glutamate, reported high conversions and low coagulum contents for the batch polymerization of lauryl methacrylate; although in their case a poly(ethylene glycol)-based inisurf was also necessary to achieve this result.

Both results point towards the use of more hydrophobic, lower CMC emulsifiers as being one of key elements for polymerizing superhydrophobic monomers in emulsion polymerization. However, in the case of Tauer et al.^[2], only an experiment involving a specific combination of a polymeric initiator and a hydrophobic emulsifier allowed the successful polymerization of lauryl methacrylate at 20 wt% solids, which is unfortunately insufficient to draw meaningful conclusions. On the other hand, while Avramidis and Bassett provide more data and also present a broader claim, the examples reported

only cover the polymerization of VeoVa monomers, which can be homo and co-polymerized in emulsion polymerization using conventional surfactants and initiation systems.^[3,4] The question of “if” superhydrophobic monomers can be polymerized under the constraints defined in this thesis has only been partially answered, while the deeper question of “how” to accomplish this feat remains completely open. The overarching objective of this chapter will be to answer the latter question.

In this work, the term “very hydrophobic” is used to refer to monomers with water solubility in the range of VeoVa 10, while the main interest lies on the polymerization of monomers regarded as “superhydrophobic”, i.e. monomers with water solubilities at least one order of magnitude below that of VeoVa 10. Lauryl methacrylate, from now on abbreviated as LMA, will be regarded as a “superhydrophobic” due to its classification as “too insoluble” in water at 60 °C according to Chai and coworkers.^[5] Both the homopolymerization and copolymerization of this monomer, with either conventional or other superhydrophobic monomers and under batch and semi-batch feeding strategies, will be investigated in a sequential fashion paying close attention to the role of the surfactants involved.

2.2. EXPERIMENTAL

2.2.1. MATERIALS

The monomers lauryl methacrylate (LMA, 96 wt% rest on isomers, Sigma-Aldrich), isobornyl acrylate (IBA, technical grade, Sigma-Aldrich), n-butyl acrylate (BA, technical grade, Quimidroga), methyl methacrylate (MMA, technical grade, Quimidroga) and methacrylic acid (MAA, 99 wt%, Sigma-Aldrich) were used as supplied without any additional purification steps. The emulsifiers used in this chapter were sodium lauryl sulfate (SLS, ≥ 98.5 wt%, Sigma-Aldrich), Dowfax 2A-1 (D2A1, 45 wt% in water, Dow), Aerosol TR-70 (TR70, 70 wt% in water/ethanol, Cytec) and Aerosol A-102 (A102, 30 wt% in water, Cytec). A summary of the main monomers and emulsifiers used in this chapter and their relevant characteristics are presented in **Error! Reference source not found.** and **Table II - 2**, respectively.

Radical initiation was primarily provided by a redox system. A 70 wt% aqueous solution of t-butyl hydroperoxide (TBH, Sigma-Aldrich) was used as oxidant, while either ascorbic acid (ASA, 99% ACROS) or Bruggolite 6M (FF6, Brüggemann) were used as reductants. Thermal initiators, azobisisobutyronitrile (AIBN, ≥ 97 wt%, Fluka) and azobis-4-cyanopentanoic

acid (V501, ≥ 75 wt%, Fluka) were also utilized in a few polymerizations. Hydroquinone (99%, Panreac) was used for stopping the polymerization in the samples withdrawn from the reactor. Double deionized water (MilliQ standards) was used in all the experiments.

Table II - 1. Summary of the monomers used and their relevant properties

Monomer	Abbreviation	Water solubility 60°C (ppm) ^[5]	Glass transition temperature [T_g] (°C)
Lauryl methacrylate	LMA	“too insoluble”	-46 ^[6]
Isobornyl acrylate	IBA	3.12	90 ^[7]
n-Butyl acrylate	BA	3380	-52 ^[8]
Methyl methacrylate	MMA	22500	125 ^[6]

Table II - 2. Summary of the emulsifiers used and their relevant properties

Emulsifier	Description	Critical micelle concentration* (ppm)	Provider
SLS	Sodium lauryl sulfate	2300	Sigma-Aldrich
Dowfax 2A-1	Alkyldiphenyloxide Disulfonate	325	Dow
Aerosol A-102	Disodium ethoxylated alcohol (C ₁₀ -C ₁₂) half ester of sulfosuccinic acid	161	Cytec
Aerosol TR-70	Sodium bistridecyl sulfosuccinate	3	Cytec

*: Determined by means of surface tension measurements

2.2.2. SYNTHESIS OF POLYMER DISPERSIONS

The procedures described in this section are meant to be general descriptions of the experiments and setups utilized in this thesis. Detailed recipes and procedures implemented will be described throughout this manuscript in the sections where they are most relevant.

Polymer dispersions were prepared by emulsion polymerization under batch and semi-batch strategies, in two available polymerization setups. The first setup involved a jacketed glass reactor equipped with a stainless steel stirrer and a glass reflux condenser. The cover of the reactor was made of stainless steel and had multiple connections for a sampling device, a nitrogen inlet, a temperature probe, and up to three different feeds for which a variety of pumps were readily available. An external water bath was connected to the reactor's jacket and used to adjust the reaction temperature. Precision balances were available to monitor the mass fed through the semi-batch feeds. Their output, as well as the input and output parameters of the pumps and water bath were all connected to an automatic control system, Camile TG (CRW Automatic Solutions), to adequately control the reaction temperature and inlet flow rates of the multiple feeds. A general scheme of polymerization setup one is presented **Figure II - 1**.

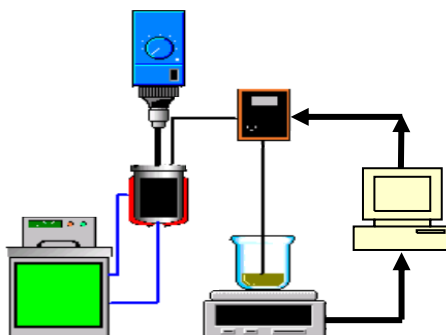


Figure II - 1. General scheme of the polymerization setup 1

The second polymerization setup was a commercially available Multiplant M100 system (Chemspeed). It included six small metallic reactors with a maximum capacity of 80 mL and anchor-shaped stirrers. Cold water was flowed through the neck at the top of the reactors, acting as reflux condenser, while heating was provided by electrical resistances, and cooling by a controlled flow of silicone oil refrigerated in an external thermostat (Huber Unistat Tango). The reactors had multiple connections for a temperature probe, nitrogen inlet and up to three semi-batch feeds supplied by syringe pumps. The reaction temperature and feeding profile were controlled through an external computer running the accompanying software. While the semi-batch feeds were controlled by volume displacement, the weight losses of the feeding vessels were also monitored in an external precision balance. A picture of the equipment used in this work is presented in **Figure II - 2**.

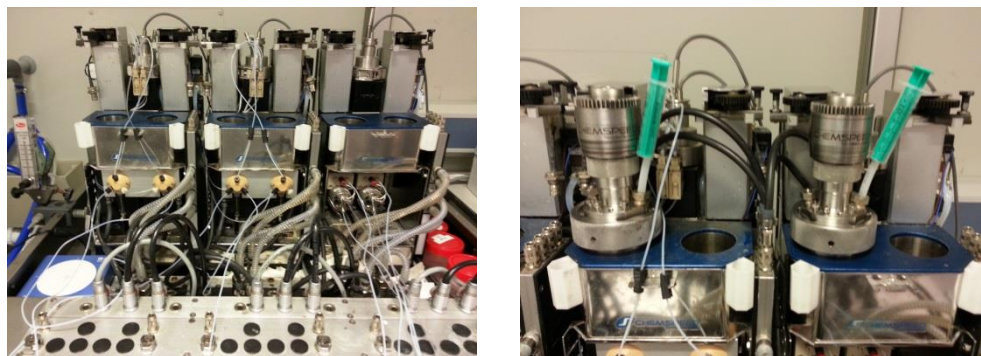


Figure II - 2. Chemspeed Multiplant M100 setup and two prepared reactors

In batch polymerizations, an initial charge of water and emulsifier was added to the reactor and stirred at 200 rpm for about 10 minutes under a nitrogen flow of 10 mL/min. The monomer or monomer mixture was then charged into the reactor and kept under continued stirring and nitrogen flow for an additional 20 minutes. The reactor temperature was raised to 70 °C and the initiator was either added, in the case of thermal initiators, or slowly fed during the polymerization in the case of redox initiators. In both cases, this point marked the beginning of the polymerization. The reaction was kept at 70°C during 180 minutes, before cooling down the reactor to room temperature and filtering the resulting latex with a filter with a pore size of 80 µm.

Semi-batch polymerizations were carried out by initially dispersing a previously prepared polymer seed in the initial charge of the reactor, under continuous stirring and nitrogen flow during at least 30 minutes. The reactor

was heated up to 70 °C, at which point a monomer mixture, either as neat monomer or in a pre-emulsion, was slowly fed for a period of 180 minutes. An additional stream containing the oxidant of a redox initiation pair was fed simultaneously during this period, while the reductant of said pair was either already inside the reactor or fed in the pre-emulsion stream. A batch period of 60 minutes took place after the end of the pre-emulsion feed, followed by cooling down of the reactor to room temperature and filtering of the resulting latex.

Batch miniemulsion polymerization was occasionally implemented. In these cases, a coarse pre-emulsion of monomer, water and emulsifier was prepared in a beaker under continuous magnetic-bar stirring for a period of 30 minutes. The pre-emulsion was then ultrasonified using a 450 W Branson sonifier (amplitude 80 and energy pulsed at 1 Hz) for a period of 20 minutes, in an ice bath to avoid overheating of the sample. The newly formed miniemulsion was then transferred to a reactor, heated to reaction temperature under a nitrogen atmosphere, and polymerized for 180 minutes by addition of a suitable initiation system.

During all the reactions, approximately 1 mL of sample was taken at regular intervals from the reactors, and the polymerization was stopped by addition of a drop of a 1 wt% aqueous solution of hydroquinone. These samples were then submitted to multiple characterization techniques described below.

2.2.3. CHARACTERIZATION OF POLYMER DISPERSIONS

Monomer conversion:

Monomer conversion was determined by gravimetric analysis and confirmed by $^1\text{H-NMR}$ analysis for the less volatile superhydrophobic monomers. Approximately 0.5 g of sample was used for the gravimetric analyses that were carried out in two drying stages: i) at 60 °C during 24 hours at atmospheric conditions, and ii) at 100 °C during 24 hours under vacuum (1 mmHg). The $^1\text{H-NMR}$ tubes were prepared with 300 μL of the sample and 300 μL of a 1 g/L solution of trimesic acid (95%, Sigma-Aldrich) in D_2O as internal standard. The conversion was followed by monitoring the disappearance of the characteristic chemical shifts of the olefinic protons of the monomers studied and comparing said signals to a calibration curve. Good agreement was always found between the gravimetric and $^1\text{H-NMR}$

analyses, suggesting the high temperature vacuum conditions applied were sufficient to completely volatilize the residual monomers.

Monomer conversions were reported by using two different conventions, i.e. overall and instantaneous conversions. The overall monomer conversion (x_o) was defined as the ratio of the polymer present in the reactor at a given time and the total monomer to be used in the formulation (Equation II - 1). The instantaneous monomer conversion (x_i) was the ratio of polymer present in the reactor and the monomer fed up to that specific time (Equation II - 2). Both values were adequately corrected for the mass withdrawn from the reactor in each sample.

$$X_o = \frac{W_{p,t}}{W_{m,total}} \quad \text{(Equation II - 1)}$$

$$X_i = \frac{W_{p,t}}{W_{m,t}} \quad \text{(Equation II - 2)}$$

Average particle size and particle size distribution:

The volume average particle size was measured mainly by dynamic light scattering (DLS) using a Zetasizer Nano ZS equipment (Malvern Instruments) at 25 °C. Before the analysis, the obtained latexes were diluted with deionized

water to an acceptable count ratio in order to avoid multiple scattering. Three consecutive runs of 12 measurements of 10 seconds each were carried out to optimize statistical relevance, and the average of these runs was reported in this thesis. The *PDI* index (\mathcal{D}), defined as twice the dimensionless ratio of the first two coefficients of the polynomial used to fit the logarithm of the correlation function, is used as a measure of the width of the size distribution. This variable can take values from 0 up to 1.0, where a sample whose *PDI* index is below 0.150 can be regarded as monodisperse.

Particle size distributions were determined by two techniques: capillary hydrodynamic fractionation (CHDF) and disc centrifuge photosedimentometry (DCP). CHDF analyses were conducted in a CHDF 2000 apparatus (Matec Applied Sciences) using a low ionic strength carrier at a flow of 1.4 mL/min and a UV detector at a wavelength of 200 nm. Each analysis lasted 17 minutes and used sodium benzoate ($\geq 99.5\%$, Sigma-Aldrich) as a marker. DCP analyses were carried out in a BI-DCP equipment (Brookhaven) using water as spin fluid and methanol as buffer fluid, and a tungsten-halogen lamp at a wavelength of 650 nm for the detection of sedimenting particles. The disc speed and spin fluid volume were adjusted according to the samples

analyzed in order to maximize the resolution of the distributions and minimize analysis time.

The number of particles was calculated from volume average particle sizes reported by the techniques described above, and the polymer mass present in the reactor determined by conversion measurements, using the following equation:

$$N_p = \frac{6w_p}{\pi\rho_p d_v^3} \quad (\text{Equation II - 3})$$

where w_p is the polymer mass (g), ρ_p is the density of the polymer particles (g/cm³) and d_v is the volume average particle diameter (cm). N_p will be reported in a volumetric basis (dm⁻³), where the reference volume is that of the final latex.

Gel content:

The gel content, or rather the fraction of insoluble material, was determined by Soxhlet extraction of the dried polymer using tetrahydrofuran (THF, technical grade, Scharlab) for a period of 24 hours. The separated insoluble fraction recovered was considered to be a crosslinked polymer network and

the ratio between its mass and total polymer mass was reported as gel content.

Average molecular weight:

Average molecular weights of the soluble polymer obtained from the Soxhlet extractions were determined by gel permeation chromatography (GPC). The samples were dried and re-dissolved in THF (HPLC grade, Scharlab). The new solutions were filtered (pore size of 0.45 μm) before injection into the GPC equipment, which consisted of a pump (Shimadzu LC-20AD), three columns (Styragel HR2, HR4 and HR6) and a refractive index detector (Waters 2410). Chromatograms were obtained at 35 $^{\circ}\text{C}$ using a THF flow rate of 1 mL/min and the obtained molecular weights were related to a calibration prepared with polystyrene standards.

Differential scanning calorimetry:

The glass transition temperatures, T_g , of the polymers prepared were determined using a differential scanning calorimeter (DSC, Q1000, TA instruments). A scanning cycle consisted of an initial cooling to -70 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, a stabilizing period of 2 minutes at this temperature, followed by a heating ramp at 10 $^{\circ}\text{C}/\text{min}$ up to 120 $^{\circ}\text{C}$. Two cycles were performed for each

sample, the first having the objective of removing the thermal history of the sample. The chromatograms reported in this thesis correspond to the second cycle. Initial estimates of the copolymer glass transition temperatures were obtained by using the Fox equation^[9]:

$$\frac{1}{T_g} = \sum_i \frac{x_i}{T_{g,i}} \quad (\text{Equation II - 4})$$

where T_g refers to the final copolymer, $T_{g,i}$ is the glass transition temperature of homopolymer of monomer i , and x_i is the weight fraction of said monomer.

Critical micelle concentration and emulsifier parking area:

The CMC of the emulsifiers was determined by surface tension measurements performed on a KSV Sigma 70 apparatus (KSV Instruments) via the Du Nouy ring method. The process involved a titration with an emulsifier solution of known concentration until micelles appeared in the system. The presence of micelles was detected as a sudden change of the slope of the surface tension with the logarithmic of the concentration of emulsifier. In the presence of polymer particles, this change was detected at higher concentrations due to the increased availability of fresh surface area to

be stabilized by emulsifier molecules prior to micelle formation. Having these two values, the parking area can be calculated through the following equation:

$$a_s = \frac{A_p}{V(CMC_p - CMC)} \quad (\text{Equation II - 5})$$

where V is the volume of the liquid phase (L), A_p the total surface area of the polymer particles (m^2), CMC_p is the concentration of emulsifier at the point in which micelles appeared in the diluted latex, and CMC is the critical micelle concentration.

2.3. LMA HOMOPOLYMERIZATION

While homopolymerization of any given monomer is rarely used in the coatings industry, mostly due to the necessity of achieving a balance between mechanical properties and optimal film formation while minimizing coalescing agents,^[10] it was used as a starting point in this work to evaluate the technical feasibility of homopolymerizing superhydrophobic monomers based on the claims previously found in the open literature. Lauryl methacrylate was the monomer of choice due to its superhydrophobic character and its liquid state at room temperature.

2.3.1. BATCH POLYMERIZATIONS

A simple batch emulsion polymerization system was utilized to test different surfactants and radical initiation systems individually and in combination. A summary of the recipes used for the batch polymerizations of LMA is presented in Table II - 3.

Table II - 3. Batch emulsion homopolymerization of LMA

Variable	Value	Variable	Value
Temperature	70 °C	Emulsifiers used	<ul style="list-style-type: none"> • SLS • TR70
Stirring rate	200 rpm		
Polymerization time	180 minutes		
Monomer content	25 wt%	Initiators used	<ul style="list-style-type: none"> • V501 • TBH/ASA • AIBN
Emulsifier content	2 wt%*		
Initiator content	1 wt%*		
Redox mol ratio	2.0 TBH/ASA		

*: Based on monomers

An initial attempt to polymerize this monomer using a conventional surfactant, sodium lauryl sulfate, was made in order to further establish the challenges imposed by the polymerization of superhydrophobic monomers. In the experiments with water soluble V501 (neutralized with sodium hydroxide) and the water soluble TBH/ASA redox pair, high amounts of residual monomer and phase separation was observed a few minutes after the samples were

taken from the reactor, making conversion and particle size measurements not reproducible, which suggested polymerization did not take place. These results were not in agreement with those found by Tauer et al.^[2], where polymerization was achievable although the final product was a rather unstable dispersion. The difference between both findings probably lied on the stabilization provided by the initiators used by these authors; either ionic stabilization from sulfate groups when potassium persulfate was used, or steric stabilization when polyethoxylated azo-initiators were used. Both stabilization mechanisms would be significantly hindered when using either V501 or the redox pair TBH/ASA.

On the other hand, the batch experiment where AIBN was used as initiator resulted in almost complete coagulation of the reaction mixture, suggesting that besides stabilization, radical initiation in the aqueous phase or radical entry in (presumably) micron-sized, colloidally unstable monomer droplets was a limiting step in the previous experiments with water soluble initiators. Due to the high amount of coagulum and also presence of some residual monomer, it was not possible to determine accurately the coagulum percentage by filtration, although visual observation showed that it would be at least 80% of the total polymer. Taking into account the heterogeneity of the

system, the samples taken from the reactor were not representative, which is why only the results obtained from the characterization of the fraction of the final latex that was possible to filter are reported in Table II - 4.

Table II - 4. Characterization of the filtered latex obtained from the homopolymerization of LMA with SLS as emulsifier and AIBN as initiator

Variable	Value
Coagulum (80 μm filter)	>80 wt%*
Particle size (d_v , \bar{D} , DLS)	553 nm (0.359)
Molecular weight (Mw, GPC)	2.7 $\times 10^4$ Da (9.1 $\times 10^3$ Da)**

*: Based on visual observation

**: Measured in the coagulum

Both the coagulum and the filtered latex were found to be completely soluble in THF through Soxhlet extraction. The relatively low average molecular weight reported could be attributed to polymerization taking place primarily in a non-compartmentalized system, similar to a bulk polymerization, where multiple radicals would coexist in the micron-sized monomer droplets that would eventually coagulate. The smaller fraction of dispersed particles that made up the filtered latex could find its origin on monomer broken off from larger droplets by stirring, stabilized against coalescence by the available

surfactant. The relatively large \mathcal{D} factor also suggested a broad particle size distribution that would support this hypothesis.

Quite similar results were found for the batch polymerizations where TR70 was used as emulsifier, even at emulsifier contents as high as 4.5 wt% based on monomer, and hence are not reported here. Water soluble initiators resulted in virtually no polymerization while oil soluble AIBN produced large amounts of coagulum. Following Avramidis and Bassett^[1] general rule of employing a low CMC hydrophobic emulsifier did not produce a stable latex in batch conditions; however, their examples for VeoVa monomers involved semi-batch polymerizations with multiple emulsifiers used simultaneously. Consequently, this strategy was adopted in a new series of polymerizations.

2.3.2. SEMI-BATCH POLYMERIZATIONS

In order to conduct semi-batch homopolymerizations of LMA, a polymer seed was required. From a polymer composition point of view, it was desirable to use a poly(LMA) dispersion as seed; however, due to the difficulties encountered in producing said polymer seed by emulsion polymerization, batch miniemulsion polymerization was used instead. The target solids

content was 40 wt%. Dowfax 2A-1 was used as emulsifier and TBH/ASA as redox initiation pair. The general procedure described for miniemulsion polymerization in section 2.2.2 was followed. The details of the polymerization are reported in Table II - 5

Table II - 5. Batch miniemulsion homopolymerization of LMA

Stage	Variable	Value	Latex characterization	
Initial Charge	Temperature	70 °C	Droplet size	321 nm
	Stirring rate	200 rpm	(d_v , \mathcal{D} , DLS)	(0.254)
	LMA content	40 wt%	Particle size	257 nm
	D2A1 content	2 wt%*	(d_v , \mathcal{D} , DLS)	(0.153)
	Redox mole ratio	2.0 TBH/ASA	Gel content (THF, Soxhlet)	82 wt%
Initiator Feed	TBH content	1 wt%*	Molecular weight (Mw, GPC)	2.8 x10 ⁵ Da
	Feeding time	120 minutes		
Batch	Batch time	60 minutes		

*: Based on monomers

Complete conversion was achieved and no coagulum was recovered from this latex. A significant reduction from the miniemulsion average droplet size to the final latex average particle size was observed, as previously reported for a similar system.^[11] Said reduction amounted to a ratio of 1.82 between the number of polymer particles and monomer droplets once their density differences were considered, although based on the \mathcal{D} indexes encountered both size distributions were found to be broad. Additionally, high gel contents

and molecular weights orders of magnitude above those found for the emulsion polymerization process when AIBN was used were determined. Clearly, miniemulsion polymerization provided a viable way to polymerize superhydrophobic monomers, even at relatively high solids contents.

The above described latex was used as seed in the semi-batch homopolymerization of LMA.

Table II - 6 summarizes the recipe and its relevant characterization data. The LMA polymer seed and the reductant ASA were placed in the initial charge of the reactor, purged with nitrogen and heated to reaction temperature. The low CMC emulsifier, TR70, was dissolved in a neat monomer feed. Simultaneously, a separate feeding stream containing emulsifier A102 and oxidant TBH was prepared. Both feeds were started simultaneously and maintained for a period of 180 minutes, followed by a batch period of 60 minutes.

High coagulum content was obtained, making it difficult to accurately quantify monomer conversion; however, unlike the batch emulsion polymerization using the redox pair TBH/ASA as initiator, no evidence of residual monomer was found through $^1\text{H-NMR}$ in the filtered latex.

Table II - 6. Seeded semi-batch emulsion homopolymerization of LMA

Stage	Variable	Value	Latex characterization	
Initial Charge	Temperature	70 °C	Coagulum (80 µm filter)	77 wt%
	Stirring rate	200 rpm		
	LMA polymer seed	7 wt%*	Particle size of the filtered latex (d_v , DLS)	230 nm
	Redox mole ratio	2.0 TBH/ASA		
Monomer Feed	Total LMA content	20 wt%	Gel content (THF, Soxhlet)	28 wt% (37 wt%)**
	TR70 content	0.8 wt%*		
	Feeding time	180 minutes	Molecular weight (Mw, GPC)	1.5 x10 ⁵ Da 9.3 x10 ⁴ Da**
Initiator Feed	TBH content	1 wt%*		
	A102 content	0.8 wt%*		
	Feeding time	180 minutes		
Batch	Batch time	60 minutes		

*: Based on monomers

**: Measured in the coagulum

A fraction of the polymer, in both the dispersed particles and in the coagulum, was insoluble in THF in proportions higher than what could be attributed to the polymer seed. The molecular weights of the soluble fraction were in the same order of magnitude as those found in miniemulsion polymerization. The results showed that, even though it was possible to polymerize lauryl methacrylate in emulsion polymerization, the latex obtained was not colloidally stable. These findings are meant to be interpreted as a positive proof of concept regarding the homopolymerization of a superhydrophobic

monomer, while the problem of colloidal stability will be addressed separately throughout this chapter.

There are multiple ways of improving stabilization of a given polymer colloid, e.g. through a different surfactant selection or by increasing the surfactant loading of the system. Additionally, it is well-known that stabilizing less hydrophobic polymers results in much higher emulsifier parking areas for anionic emulsifiers like SLS,^[12-15] making these surfaces effectively easier to stabilize. Similar results have also been observed by modifying a hydrophobic polymer phase like polystyrene through copolymerization with less hydrophobic monomers like methyl methacrylate, either in a homogenous^[13] or in a structured way.^[12] Taking this into consideration, in the next section the copolymerization of LMA with less hydrophobic conventional monomers will be put into practice

2.4. LMA/BA/MMA COPOLYMERIZATIONS

The great majority of commercial emulsion polymers are indeed copolymers for the reasons previously exposed. Because of this, most industry-oriented works related to polymerization of superhydrophobic monomers have gone

directly to copolymerization, more specifically, the incorporation of these special monomers in well-known polymer matrices as a mean to further improve the performance of existing commercial products.^[16,17] Ideally, a randomly distributed copolymer of conventional and superhydrophobic monomers would be obtained, in a flexible system where other parameters such as particle morphology, latex rheology and surface chemistry could also be easily controlled.

In this section, copolymerization will be used to improve colloidal stability while attempting to maximize the content of superhydrophobic monomers in the polymer matrix, with the specific objective of establishing a polymer system that could provide relevant information of the polymerization of the superhydrophobic monomers.

A semi-batch emulsion polymerization strategy will be used as reference. Lauryl methacrylate will be copolymerized with butyl acrylate and methyl methacrylate, two of the most well-known conventional acrylate monomers in emulsion polymerization. Two sets of experiments were performed based on the amount of superhydrophobic monomer used: i) low LMA content polymerizations, ranging from values of 5 to 20 wt% based on total

monomers, and ii) high LMA content polymerizations, starting at 50 wt% based on total monomers. The remaining monomers, BA and MMA were maintained at a fixed 50/50 molar ratio. A result-based reasoning was utilized to implement this classification, as it will be explained throughout this section.

Table II - 7. Semi-batch LMA/BA/MMA copolymerizations

Stage	Variable	Value
Initial Charge	Temperature	70 °C
	Polymer seed	4 – 7 wt%*
Pre-Emulsion	Monomer content	40 wt%
	LMA content	5 – 70 wt%*
	BA/MMA mole ratio	50/50
	TR70 content	0.45 wt%*
	TR70/SLS ratio	1.0/0.6 wt
	Redox mole ratio	2.0 TBH/ASA
	Feeding time	180 minutes
Oxidant Feed	TBH content	0.7 wt%*
	TR70/A102 ratio	1.0/1.0 wt
	Feeding time	180 minutes
Batch	Batch time	60 minutes

*: Based on monomers

A summary of the relevant aspects of the recipes implemented in the LMA/BA/MMA semi-batch emulsion copolymerizations is reported in Table II - 7. Some changes were implemented with respect to previous LMA homopolymerizations. The neat monomer feeding stream was replaced by a

pre-emulsion feed, and SLS was added to the emulsifier mixture to improve both the stability of the pre-emulsions and the eventual latexes.

Two new polymer seeds with a 50/50 BA/MMA molar ratio were synthesized sequentially; the first one being prepared through batch emulsion polymerization at 20 wt% solids content, using TBH and ASA as redox initiation pair, and SLS as emulsifier. The contents of TBH and SLS were 0.7 and 1.0 wt% based on monomers, respectively, and ASA was adjusted to keep a 2.0 TBH/ASA molar ratio. The reaction was carried out at 70 °C, with the oxidant and reductant being fed separately during a period of 180 minutes, followed by an additional 60 minutes at reaction temperature. The resulting polymer seed had an average particle size of 89 nm and a D index of 0.037, and will be referred to as BMS throughout this section.

The second BA/MMA polymer seed was prepared through semi-batch emulsion polymerization at 40 wt% solids content, using the BMS polymer seed at an addition level of 7 wt% based on monomer. The recipe detailed in Table II - 7 was followed, with the exception that no LMA was added to the monomer mixture. The final latex had an average particle size of 252 nm with a D index of 0.098, and will be referred to as BML throughout this section.

High conversions were determined gravimetrically and virtually no coagulum was recovered in the making of both BMS and BML polymer seeds. The new BMS and BML seeds, as well as the previous LMA polymer seed, were utilized independently in the following semi-batch copolymerizations, at different levels and with variable contents of LMA.

Table II - 8. Coagulation data of the LMA/BA/MMA copolymerizations

Reaction	Polymer seed	$N_{P,Seed}$ (dm^{-3})	Seed content*	LMA content*	Coagulum**
BMS-H-5	BMS	5.7×10^{16}	7 wt%	5 wt%	<1.0 wt%
BMS-H-10	BMS	5.7×10^{16}	7 wt%	10 wt%	<1.0 wt%
BMS-H-20	BMS	5.7×10^{16}	7 wt%	20 wt%	<1.0 wt%
BMS-H-50	BMS	5.7×10^{16}	7 wt%	50 wt%	34 wt%
BMS-H-70	BMS	5.7×10^{16}	7 wt%	70 wt%	57 wt%
LMA-M-50	LMA	2.6×10^{15}	7 wt%	50 wt%	2.1 wt%
LMA-M-70	LMA	2.6×10^{15}	7 wt%	70 wt%	26 wt%
LMA-L-70	LMA	1.3×10^{15}	4 wt%	70 wt%	1.4 wt%
BML-L-70	BML	1.7×10^{15}	4 wt%	70 wt%	0.9 wt%

*: Based on monomers

** : Based on total polymer

Not every permutation of the variables listed in Table II - 7 lead to an executed polymerization either due to lack of colloidal stability of previous experiments and/or potential information being redundant. A compilation of the coagulation data of the polymerizations performed is presented in Table II - 8 and elaborated upon throughout this section. These experiments have been classified based on the polymer seed used, the number of initial seed particles (H for high, M for medium and L for low) and the LMA content of the final latex.

The first set of polymerizations, referred to in this work as low LMA content polymerizations, were performed using the BMS seed and are identified as BMS-H-5, BMS-H-10 and BMS-H-20. Under this particular set of conditions, polymerizations with contents of LMA up to 20 wt% resulted in stable and homogeneous dispersions with coagulum contents under 1 wt% based on total polymer, which allowed for adequate monitoring and characterization of the samples taken during the polymerizations. Figure II - 3 shows the time-evolution of the conversion (instantaneous and overall) and number of particles (calculated from DLS results) of these experiments.

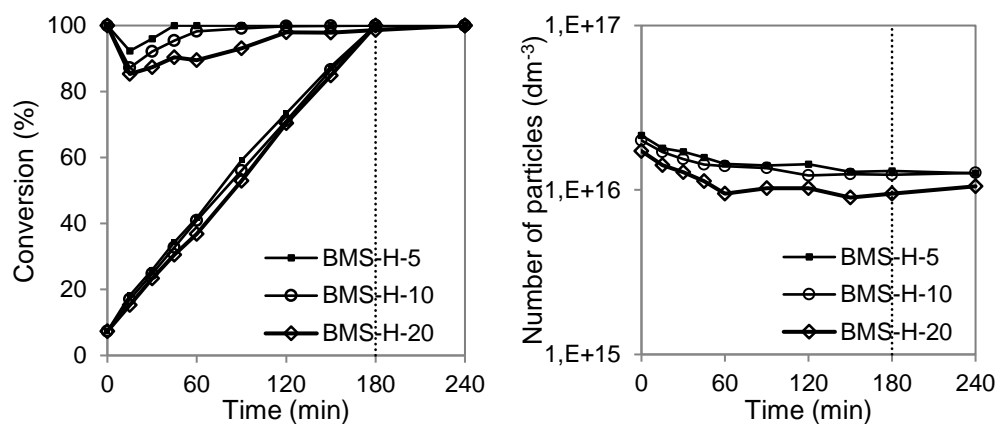


Figure II - 3. Conversion (left) & number of particles (right) time-evolutions for the low LMA content LMA/BA/MMA copolymerizations

Monomer conversions were generally high, reaching monomer starved conditions since the early stages of the polymerization and suggesting that the monomers are reacting simultaneously, even though the polymerizations were progressively slower the higher the LMA content was. It could also be observed that during the experiments particles were lost, probably due to micro-coagulation events, and that this trend was also accentuated at higher contents of LMA, suggesting that the presence of this monomer resulted in a loss of stability even at such low levels of incorporation. To further illustrate this point, polymerizations with LMA contents of 50 and 70 wt% (BMS-H-50 and BMS-H-70) reached coagulum values of 34 and 57 wt% based on polymer, respectively (see Table II - 8).

In order to further increase the content of superhydrophobic monomers while maintaining colloidal stability, a second set of experiments referred to as high LMA content polymerizations was performed, in which a lower total surface area of the final latex was targeted by adjusting the number of seed polymer particles. This adjustment was achieved by using the larger polymer seeds (LMA and BML, instead of BMS) and/or lower seed polymer content (4 instead of 7 wt% based on monomers).

Using the LMA seed while maintaining the seed content constant allowed for a reduction in the number of particles from 5.7×10^{16} to $2.6 \times 10^{15} \text{ dm}^{-3}$, which resulted in a decrease on the coagulum content from 34 to 2.1 wt% at 50 wt% LMA (LMA-M-50), and from 57 to 26 wt% at 70 wt% of LMA (LMA-M-70). Lowering the number of particles further by dropping the LMA seed content to 4 wt% based on monomer reduced the coagulum contents to less than 1.5 wt%, even for the highest LMA contents (LMA-L-70). Similar results were also found for a comparable number of seed polymer particles when the BML seed was used (BML-L-70), suggesting that the effect of the polymer seed nature on colloidal stability was not significant.

The time-evolution of the conversions for the high LMA content polymerizations with relatively low coagulum contents (LMA-M-50, LMA-L-70 and BML-L-70) are presented in Figure II - 4.

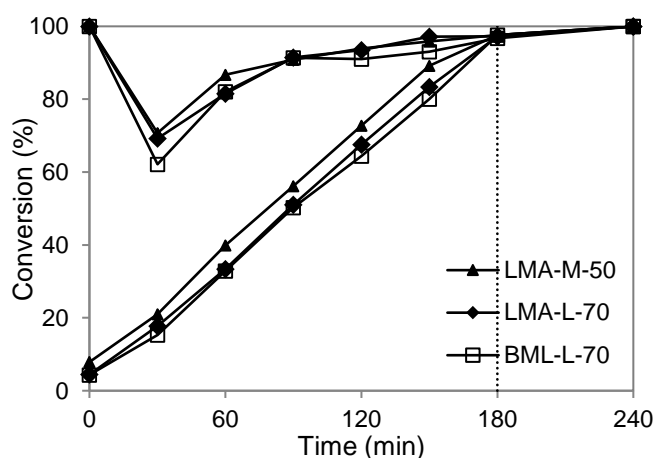


Figure II - 4. Conversion time-evolutions for the high content LMA/BA/MMA copolymerizations

The conversion progression during the reaction was slower compared to the results obtained for the low LMA content polymerizations, not achieving monomer starved conditions although complete conversions were reached at the end of the reactions. The slower development of the polymerization was expected considering the decreased number of seed particles used in order to keep coagulation values in check. No significant differences between polymerizations with LMA contents of 50 and 70 wt% were observed.

The particle size distributions (PSD) of many of the samples taken during these polymerizations were found to be broad, making average particle size measurements by DLS inadequate. To properly analyze the PSD evolution in these cases, CHDF measurements were conducted instead, and the results obtained are reported on Figure II - 5. The total area of the PSD was adjusted to the ratio between polymer mass at a given time, and final polymer mass, in order to facilitate its chronological analysis. The final latexes were found to be multimodal, for both the broad LMA and the narrow BML polymer seeds. It was possible to observe what seemed to be growth of original seed particles and continued growth of existing polymer particles during the polymerization, an event most noticeable for the BML seed in the first 30 minutes of polymerization, where the existing particle populations were displaced to higher sizes while maintaining similar distributions. There was also evidence of formation of new particles in the 200 – 300 nm range throughout the reaction, quite likely resulting on the significant increase of the instantaneous conversions observed after one hour of polymerization (see Figure II - 4).

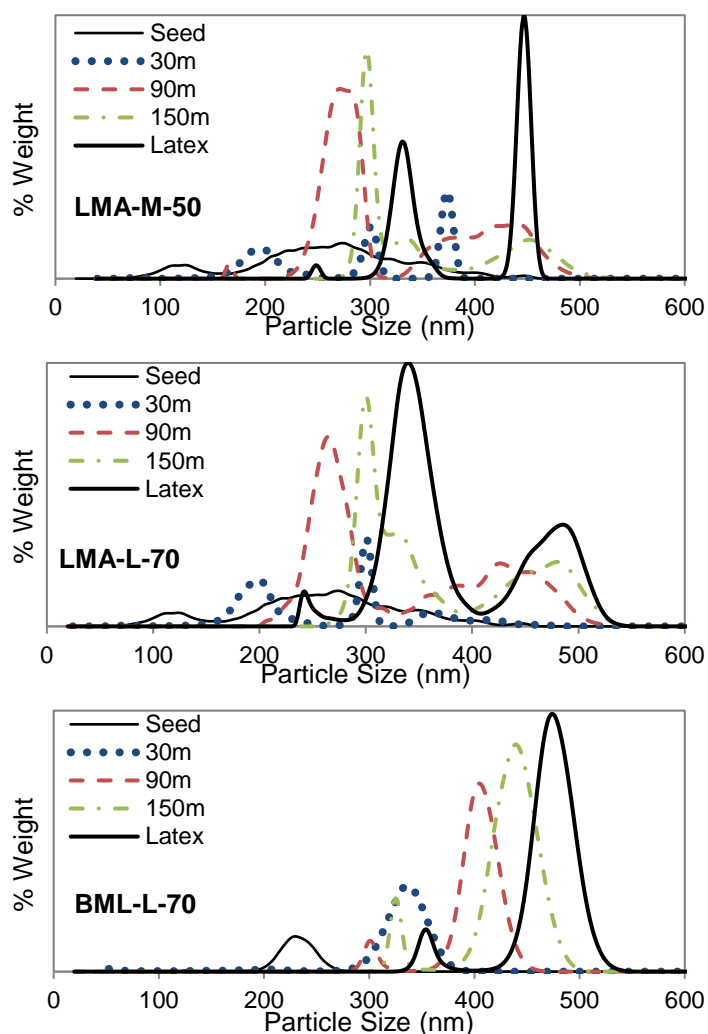


Figure II - 5. Particle size distribution time-evolutions for the high content LMA/BA/MMA copolymerizations

On the previously discussed low LMA content experiments, high conversions were observed and the number of particles were significantly more stable. Taking into account the low amounts of superhydrophobic monomer

investigated, it is possible to propose a diffusion-based monomer transport mechanism aided by the bulk of conventional monomers present in the mixture. On the other hand, in the case of the high LMA content polymerizations where conventional monomers do not represent a significant majority, particle growth is most likely taking place through a different mechanism; among which monomer transfer to particles by collisions or particle-to-particle coagulation could be viable options.^[6,18-20]

2.4.1. FILM PROPERTIES

Several films were prepared in small cylindrical silicone molds using these latexes in order to evaluate surface contact angles. Deionized water was used as the fluid of analysis. Previous to the evaluation, the films were soaked in water during three days and then dried in order to remove excess emulsifier that could compromise the experiments. Additionally, films were casted on a temperature-controlled stainless steel surface with a pre-set linear temperature profile, in order to determine the minimum film formation temperature of the latexes. The results obtained are reported in Table II - 9.

Table II - 9. Film properties of the LMA/BA/MMA copolymers

Reaction	Contact Angle	MFFT
BMS-H-5	88°	14 °C
BMS-H-10	87°	13 °C
BMS-H-20	89°	13 °C
BMS-H-50	99°	< 5 °C
BMS-H-70	94°	< 5 °C
LMA-M-50	97°	< 5 °C
LMA-M-70	99°	< 5 °C

*: Based on monomers

No significant changes were observed in both properties measured that could be associated to an increased LMA content within the 5 to 20 wt% range of the first set of polymerizations. However, high content LMA polymerizations did have a significant effect on the film hydrophobicity, expressed by the contact angle, with values reaching 99°. Due to the soft nature of LMA, polymers with contents above 50 wt% present a MFFT below 5°C, the lower end of the measuring range of the equipment utilized.

In summary, the results obtained in this section showed that through copolymerization it was possible to significantly increase the colloidal stability

of the resulting polymers at high levels of superhydrophobic monomer incorporation, for at least 40% solids content. Further efforts will be undertaken in order to tailor the expected properties of the polymer dispersions, and to acquire sufficient relevant data to properly understand the polymerization mechanism at hand.

2.5. LMA/IBA COPOLYMERIZATIONS

The latexes prepared up to this point had aimed to produce the most hydrophobic film possible by polymerizing the highest amount of superhydrophobic monomers that could produce a stable dispersion under the constraints outlined in the objectives, in which applications as coatings is desired. As a result, homopolymerization of LMA, as well as copolymerization with LMA contents up to 70 wt%, have been attempted encountering varying degrees of success. However, as mentioned earlier, poly(lauryl methacrylate) has a very low T_g , not suitable for a protective coating. Because of this, copolymerization with a higher T_g monomer was necessary in order to synthesize a copolymer with the desired properties.

Among the typical “hard monomers”, a term coined to refer to monomers whose homopolymer has a relatively high T_g , methyl methacrylate and styrene are the most common choices; yet, in order to maximize the hydrophobicity of the resulting polymer, conventional monomers should be replaced in favor of more hydrophobic alternatives. Taking this into consideration, isobornyl acrylate was selected. This monomer, besides having a T_g comparable to that of MMA, also has the lowest quantitatively measurable solubility in water reported by Chai and coworkers^[5] and it has been reported to polymerize in aqueous media in absence of energy intensive equipment.^[21]

A similar semi-batch emulsion copolymerization strategy was once again used for this series of experiments. The monomers LMA and IBA were fed as a pre-emulsion at a 50/50 weight ratio in order to target a glass transition temperature of approximately 6°C according to Fox equation (Equation II - 4). Emulsifiers TR70 and SLS were fed together with the monomers in a pre-emulsion stream, while A102 was fed in a separate stream containing the oxidant. A summary of the recipe details are presented in Table II - 10.

Table II - 10. Semi-batch LMA/IBA copolymerizations

Stage	Variable	Value
Initial Charge	Temperature	70 °C
	Polymer seed	Variable
Pre-Emulsion	Monomer content	40 wt%
	LMA/IBA wt ratio	50/50
	TR70 content	0.45 wt%*
	TR70/SLS ratio	1.0/1.5 wt
	Redox mole ratio	2.0 TBH/ASA
	Feeding time	180 min
Oxidant Feed	TBH content	0.5 wt%*
	TR70/A102 ratio	1.0/2.0 wt
	Feeding time	180 minutes
Batch	Batch time	60 minutes

*: Based on monomers

Taking into account the influence of the number of polymer seed particles on the colloidal stability for the LMA/BA/MMA copolymerizations, special attention was given to tracking this property throughout the new series of LMA/IBA polymerizations to attempt to elucidate their effect on the polymerization mechanism. To that end, several isobornyl acrylate latexes were prepared through batch emulsion polymerization and later used as polymeric seeds under different circumstances. Aerosol A-102 was used as emulsifier at different levels to control the final particle size. High conversions were determined gravimetrically and virtually no coagulum was recovered in

any of the experiments. The detailed recipe and relevant characterization results are listed in Table II - 11.

Table II - 11. Recipe and characterization of the IBA polymer seeds

Stage	Variable	Value	A-102 content*	DLS (d_v, \mathcal{D})	Seed Name
Initial Charge	Temperature	70 °C	0.33 wt%	222 nm (0.049)	IBA-222
	Monomer content	25 wt%			
	A102 content	Variable			
Oxidant Feed	TBH content	0.5 wt%*	1.00 wt%	115 nm (0.035)	IBA-115
	Feeding time	60 minutes			
Reductant Feed	Redox mole ratio	2.0 TBH/ASA	3.33 wt%	66 nm (0.013)	IBA-66
	Feeding time	60 minutes			
Batch	Batch time	60 minutes			

*: Based on monomers

As an initial approach, the number of seed particles used for the successful polymerization of the previous 70 wt% LMA latexes, $1.3 \times 10^{15} \text{ dm}^{-3}$, was used as a reference. The IBA-222 seed was regarded as the most adequate to imitate those conditions as it would also allow the use a seed content of 3 wt% based on monomers to reach that number of particles, in the same order as the seed loading for reactions LMA-L-70 and BML-L-70. This first LMA/IBA reaction was identified as IBA-222-L, on account of the polymer seed used and the relatively low amount of seed particles involved.

The time-evolution of the instantaneous conversions of each monomer (determined by $^1\text{H-NMR}$) for reaction IBA-222-L, as well as the overall copolymer composition estimated from this data, are plotted in Figure II - 6. The conversions reported were in the same order as the instantaneous conversions obtained for the high LMA content LMA/BA/MMA polymerizations. The polymer composition quickly reached the expected values according to these measurements, since both LMA and IBA conversions were similar. Additionally, the coagulum contents for this polymerization did not exceed 1 wt% of the total polymer formed.

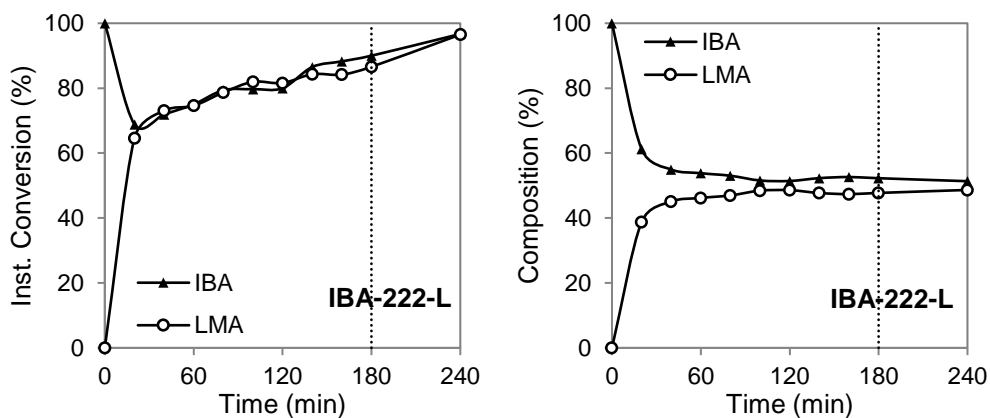


Figure II - 6. Monomer conversion (left) & copolymer composition (right) time-evolutions for LMA/IBA copolymerization IBA-222-L

The PSD evolution of this polymerization is shown in Figure II - 7. Likewise for the high content LMA/BA/MMA copolymerizations, broad/multimodal PSD

were detected in the samples taken during the reaction, requiring in this case CHDF measurements. Once again, an adjustment of the total area based on the polymer mass in the reactor was carried out to facilitate its analysis. Growth and broadening of the initial polymer seed population was evidenced during the first hour of polymerization, followed by the emergence of a new particle population during the second hour. Continued growth was once again observed towards the end of the pre-emulsion feed and until complete conversion was achieved.

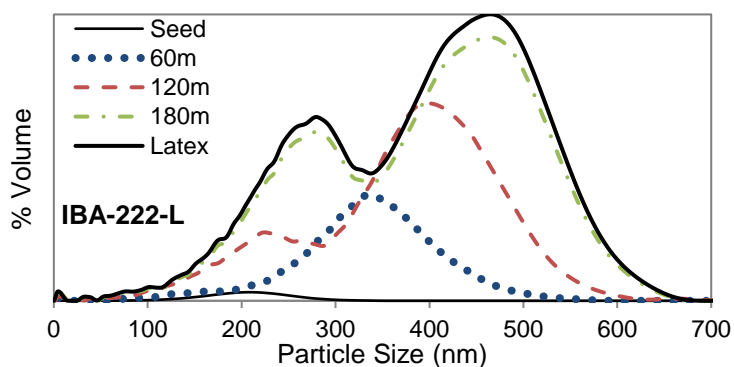


Figure II - 7. Particle size distribution time-evolution for LMA/IBA copolymerization IBA-222-L

The results obtained in this experiment were strikingly similar to those observed for all the previous high content LMA polymerizations, both in terms of conversion and particle size evolution, where the nature of the polymers

synthesized had little effect on the overall evolution of the polymerization when carried out with similar numbers of polymer seed particles.

Unlike the previously discussed high content LMA copolymerizations, it was possible to maintain colloidal stability in this new set LMA/IBA copolymerizations to a reasonable extent starting at a broader (and higher) range of polymer seed particles, while using moderate amounts of emulsifier (see Table II - 10). As a result of that, the following framework for the detailed analysis of the effect of the number of particles on the polymerization of superhydrophobic monomers was developed.

2.5.1. EFFECT OF THE NUMBER OF PARTICLES

A total of five polymerizations were conducted where the main control variables were the number of seed particles present in the reactor at the beginning of the polymerization, and the weight fraction the seed polymer represents with respect to the final polymer. To that end, the IBA-115 and IBA-66 polymer seeds were used at different levels to allow the independent study of these two variables. The recipe and procedure outlined in Table II -

10 was followed, and a summary of the polymerizations conducted under this study and their relevant data is reported in Table II - 12.

Higher coagulum contents were recovered from the reactions involving the highest number of polymer seed particles, as previously observed on the LMA/BA/MMA copolymerizations; nevertheless, the coagulum contents were considered to be low enough not to significantly compromise the data obtained from the corresponding homogeneous dispersions.

Table II - 12. Effect of the number of seed particles on the copolymerization of LMA/IBA at a 50/50 weight ratio

Reaction	$d_{p,seed}$ (nm)	$N_{p,Seed}$ (dm^{-3})	$A_{p,Seed}$ (m^2/dm^3)	Seed content*	Coagulum**
IBA-115-L	115	2.1×10^{15}	81	0.4 wt%	<1.0 wt%
IBA-115-M	115	1.0×10^{16}	430	2.0 wt%	<1.0 wt%
IBA-115-H	115	7.1×10^{16}	3052	18.5 wt%	7.0 wt%
IBA-66-L	66	2.1×10^{15}	30	0.1 wt%	2.0 wt%
IBA-66-H	66	7.1×10^{16}	853	2.9 wt%	6.0 wt%

*: Based on monomers

** : Based on total polymer

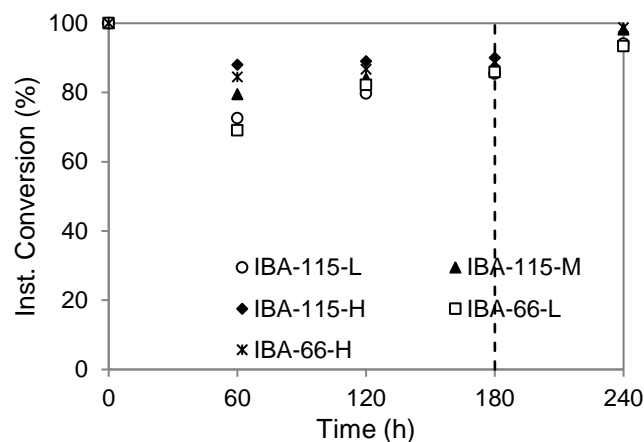


Figure II - 8. Conversion time-evolutions for the LMA/IBA copolymerizations

The evolution of the monomer conversion through time is presented in Figure II - 8, where it can be observed that increasing the number of initial seed particles lead to faster kinetics throughout the reactions (IBA-115-H and IBA-66-H); however all the experiments reached high conversions by the end of the feeding period.

The average particle sizes of the samples taken from the reactors during the polymerizations were analyzed by DLS, although the particle size distributions of the samples that reported \mathcal{D} indexes above 0.2 were subsequently determined by disc centrifuge photosedimentometry (DCP). The PSD and number of particles evolutions for reaction IBA-115-L (115 nm seed, $2.1 \times 10^{15} \text{ dm}^{-3}$ seed particles) are reported in Figure II - 9.

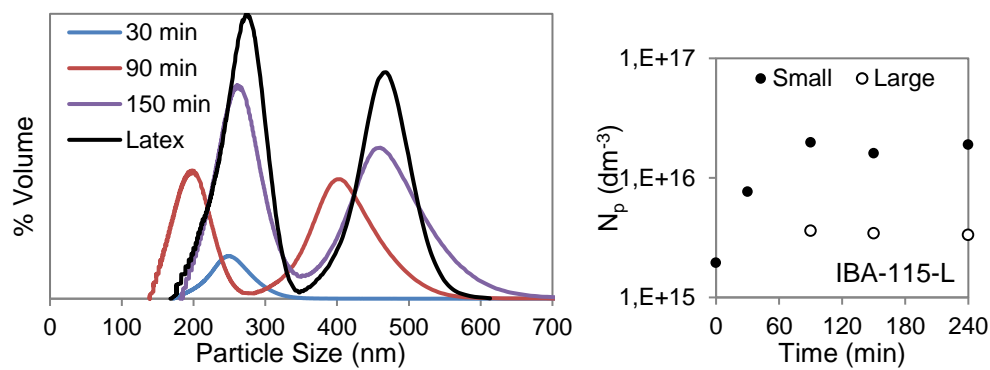


Figure II - 9. PSD and number of particles time-evolution for IBA-115-L

The seed polymer PSD was omitted since it only represented a negligible fraction of the final polymer; nevertheless, depending on the PSD of the seed, particle growth rate was affected and therefore the final PSD. The results are similar to those obtained previously (Figure II - 7), where evidence of two distinct populations can be observed along the polymerization even if the original seed particles presented a narrow particle size distribution. It can also be observed that the number of particles increased during the first half of the pre-emulsion feed, an event that can be attributed to the nucleation of a new particle population during this period of time, and then stabilized. Growth of existing polymer particles in absence of new nucleations seemed to take place from that point forward. The ratio between the number of small and large particle was ca. 5-to-1 during the second half of the polymerization, with

small particles undergoing a volumetric growth approximately three times higher than the large particles.

Figure II - 10 shows the PSD and number of particles evolution for reaction IBA-115-M. Even though a secondary particle population was not observed in this experiment, the broadening of the original distribution lead to inconsistent results by DLS. Because of that, DCP results are presented instead. Some evidence of secondary nucleations can be noted; however, the number of particles stabilized earlier in the polymerization compared to the results obtained for the previous reaction.

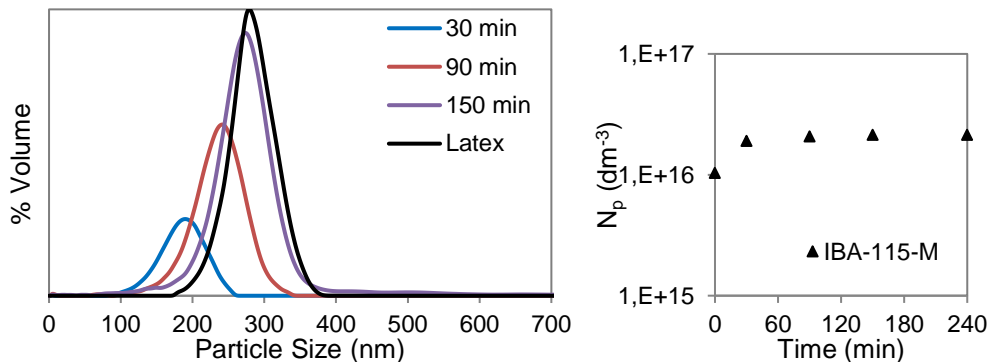


Figure II - 10. PSD and number of particles time-evolution for IBA-115-M

The results obtained for reaction IBA-115-H are reported in Figure II - 11. Unlike the previous two experiments, in this case the average particle sizes obtained by DLS were reproducible, with corresponding \mathcal{D} indexes under 0.1.

Evidence of continued growth of existing polymer particles in a single and narrow size population was ascertained, keeping a rather constant number of particles throughout the polymerization.

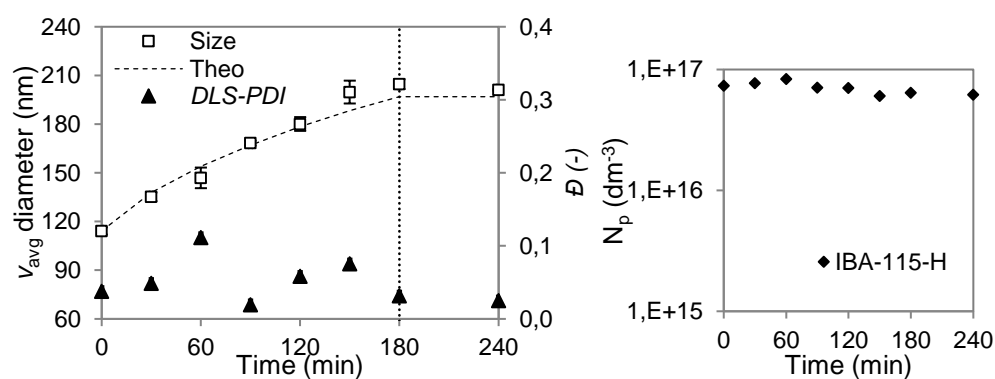


Figure II - 11. Volume average particle size (left) and number of particles (right) time-evolution for IBA-115-H

A rough estimation of the total surface area of the latexes obtained for reactions IBA-115-L and IBA-115-H reveals values of approximately 230 and 285 m^2/dm^3 , respectively. In light of these estimations and looking back at the coagulum contents reported in Table II - 12, it is possible to correlate the two considering that the latex produced by reaction IBA-115-H has approximately 24% more total surface area than the latex produced by reaction IBA-115-L, and yet the same amount of emulsifier to stabilize said area. Such differences would have a potentially significant effect on colloidal stability. A similar

comparison can be observed between reactions IBA-66-L and IBA-66-H, as will be discussed later.

Regardless of the coagulum contents, the main difference between these two polymerizations is the number and total surface area of the seed particles, which resulted in two completely different PSD for nearly identical recipes and procedures. A secondary factor that could have also accounted for the difference in PSD is the fraction the seed polymer represented on the final latex (see Table II - 12). In order to reach the high number of particles used in reaction IBA-115-H, 18.5 wt% of the final polymer would be coming from the seed particles, whereas for the low number of particles of reaction IBA-115-L, only 0.4 wt% of the final polymer would be already present in the seed.

To elucidate whether or not the amount of seed polymer in the final latex or the total surface area of the seed particles had a significant effect on the previous findings, reactions IBA-66-L and IBA-66-H were carried out. In this case, the smaller IBA seed of 66 nm was utilized, which allowed for a lower seed content and surface area to get the desired number of particles in both cases, as reported in Table II - 12. In Figure II - 12 and Figure II - 13, the evolution of the PSD for reaction IBA-66-L and the volume average particle

size evolution for reaction IBA-66-H, are plotted. The results obtained in both cases are similar to their homologues, reaction IBA-115-L and IBA-115-H. The experiment with a low number of seed particles produced a bimodal dispersion, with strong evidence of secondary particle nucleations, and the experiment with a higher number of seed particles produced a relatively monomodal latex with a very low polydispersity and a stable number of particles. The ratio between the number of small and large particles was also close to 5-to-1, but with a smaller volumetric growth ratio of 2-to-1 among them. These results confirmed yet again that the effect of the number of seed particles is the predominant factor on the final PSD obtained.

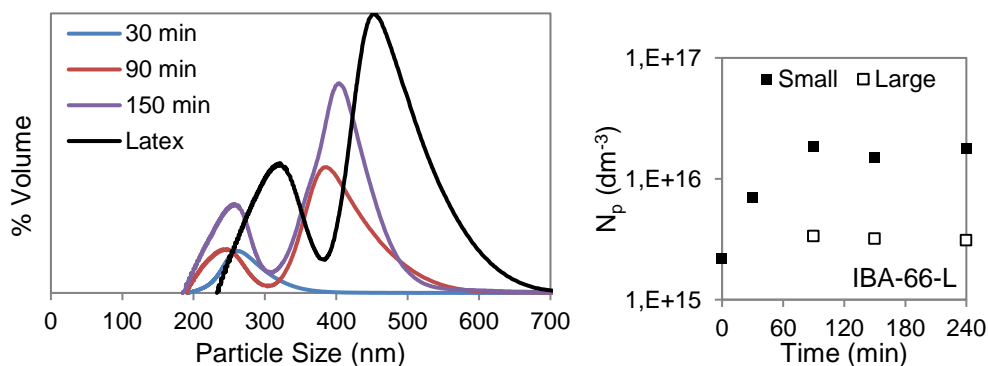


Figure II - 12. PSD and number of particles time-evolution for IBA-66-L

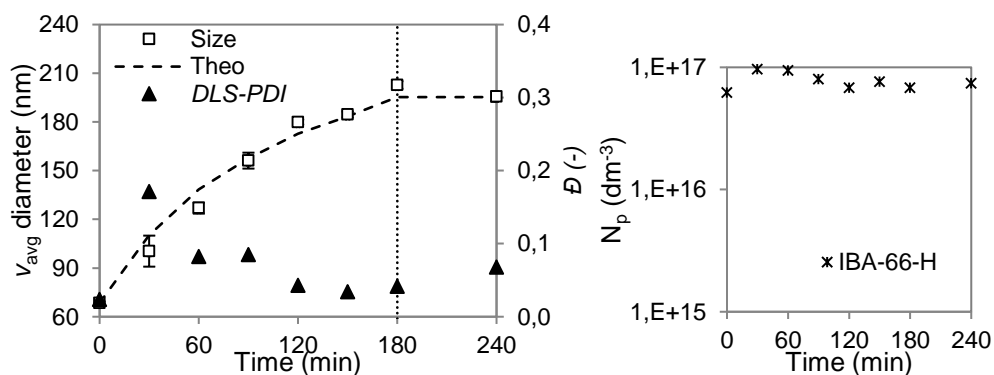


Figure II - 13. Volume average particle size (left) and number of particles (right) time-evolution for IBA-66-H

2.6. POLYMERIZATION MECHANISM

In order to provide a hypothesis for the polymerization mechanism of superhydrophobic monomers under the conditions evaluated in this chapter, it is critical to explain how these monomers could be transported in aqueous media. Based on the results obtained in this chapter, and those reviewed in literature in Chapter I,^[1,2,21] the use of hydrophobic surfactants seems to be associated with the successful emulsion polymerization of monomers like LMA and IBA. Back and Schork^[21] suggested the possibility of solubilization of oligomers through surfactant molecules as an initial step to create polymer particles, while Tauer et al.^[2] proposed a compatibilization between the monomer and the aqueous phase induced by the PEG chains on the macro azo-initiator and a hydrophobic surfactant. Additionally, Avramidis and

Bassett^[1] claimed a direct relation between the polymerization of hydrophobic monomers and the use of a hydrophobic surfactant. The potential contributions of these hypotheses will be further analyzed in this section.

2.6.1. MICELLAR SOLUBILIZATION VS DROPLET STABILIZATION

In order to elucidate the nature of the involvement on the polymerization of superhydrophobic monomers of the hydrophobic emulsifier used in this thesis, Aerosol TR-70, several emulsions were prepared at 10 wt% monomer content in water, with different emulsifier concentrations. The emulsions were stirred at 200 rpm for one hour and then allowed to stand during 24 hours. The experimental conditions followed are summarized in Table II - 13.

Table II - 13. Droplet stabilization: Experimental conditions

Variable	Value
Monomer content	10 wt%
TR70 content (Based on its CMC)	0.05 – 500 xCMC
Monomers mixtures	<ul style="list-style-type: none">• LMA• 50/50 LMA/IBA
Stirring rate	200 rpm
Stirring/Standing time	1h/24h

Two phases were distinctly observed after standing for 24 h, a top monomer phase and a bottom aqueous phase. Samples were taken from the bottom phase and submitted to $^1\text{H-NMR}$ analysis, to determine the monomer concentration, and run through DLS in order to verify if a reliable measurement of monomer droplets could be acquired. Both analyses were repeated after centrifugation at 7000 rpm during 20 minutes. The results obtained are presented in Figure II - 14.

$^1\text{H-NMR}$ analysis show that the concentration of monomer in the aqueous phase increases with the content of emulsifier used in the recipe, as expected, although the effect is significant only at concentrations of emulsifier over 100 times its critical micelle concentration. In the case of the 100% LMA emulsion, presented in Figure II - 14, the monomer concentration determined in the aqueous phase for a TR-70 concentration of 250 times its CMC was comparable to that of styrene in water at 60 °C reported by Chai et al.^[5], which is commonly regarded as sufficient to support a kinetically-controlled emulsion polymerization should diffusion be the main transport mechanism.

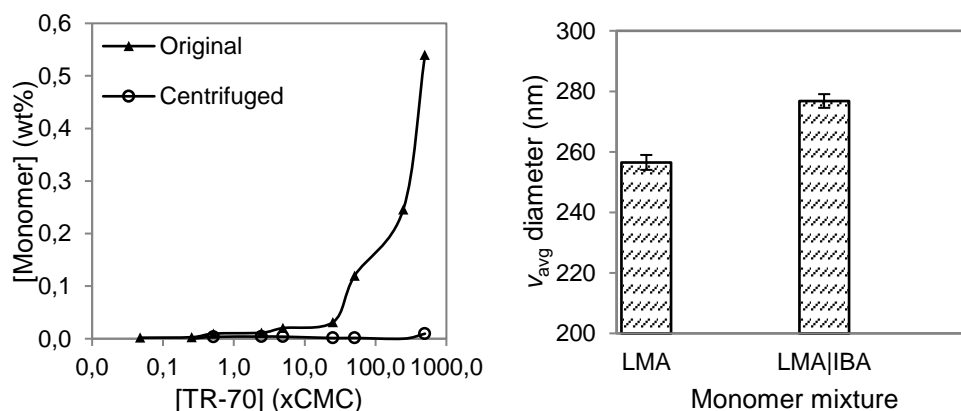


Figure II - 14. $^1\text{H-NMR}$ results for the LMA concentration in water in the emulsions with different TR-70 concentration (left) and DLS results for LMA and 50/50 LMA/IBA emulsions at a TR-70 concentration of 250xCMC (right)

Up to this point, these results could be attributed to the solubilization of monomers or oligomers suggested by several authors.^[2,21] Taking also into consideration that this effect was only observed at surfactant concentrations significantly above the CMC, said monomer solubilization could be taking place within micelles following the mechanism proposed by Carroll.^[22] In this mechanism, micelles diffuse through the aqueous phase and are adsorbed-desorbed at the oil/water interface, instead of requiring the diffusion of monomer units through the aqueous phase in order to reach and swell the micelles. This mechanism is greatly benefited by the abundance of micelles, which is consistent with the use of low CMC surfactants proposed by Avramidis and Bassett,^[1] and the use of hydrophobic surfactants and initiators observed by Tauer et al.^[2]

In order to verify if the monomer is solubilized in the aqueous phase, the samples were centrifuged, and the $^1\text{H-NMR}$ analyses repeated. If the monomer was indeed solubilized, centrifugation of the samples should have had no effect on the monomer concentration, since neither the solubilized monomer nor the micelles were large enough to sediment under such conditions. As shown in Figure II - 14, no monomer was found in the aqueous phase, indicating that the monomer was instead emulsified in this phase after centrifugation. DLS analyses of the aqueous phase, reported on the right side of Figure II - 14 for a TR70 concentration 250 times its CMC, revealed that monomer droplets with a volume-average size between 200 and 300 nm were present in the sample. Even after 24 hours of standing time, droplet size measurements by DLS showed high reproducibility.

Similar results were obtained for the 50/50 LMA/IBA monomer mixture, with slightly higher droplet sizes. This can be attributed to some extent to Ostwald ripening, considering that while IBA has extremely low water solubility, it is higher than the solubility of LMA and hence more susceptible to diffusion through the aqueous phase over a period of 24 hours. It is also worth mentioning that at lower TR70 concentrations, between 50 and 250 times its CMC, DLS measurements showed similar droplet sizes, although with lesser

reproducibility, for the LMA emulsions. On the other hand, the 50/50 LMA/IBA emulsions phase separated at the same conditions.

Attempting to prepare emulsions, either partially or completely made up of conventional monomers like styrene or VeoVa 10, resulted in the absence of monomer droplets in the aqueous phase, once again possibly due to Ostwald ripening. It was also observed that less hydrophobic emulsifiers, such as Aerosol A-102 or Downfax 2A-1, were not able to stabilize small droplets; however, it is important to notice that reaching concentrations over 100 times their CMC translated into values above 10 wt% based on monomers. These contents of emulsifier would not be viable industrially and are therefore excluded from the scope of this thesis. Additionally, at such concentrations thermodynamically stable multi-phase systems are likely to form, favoring the solubilization of monomers over their emulsification.^[23]

In summary, the use of Aerosol TR-70 promoted the stabilization of nano-sized monomer droplets when used at concentrations two orders of magnitude above its CMC. Nonetheless, by virtue of its extremely low CMC, the concentrations of emulsifier required to stabilize such droplets were well within acceptable industrial values.

2.6.2. MONOMER TRANSPORT BY COLLISIONS

It is often found in literature that, when the transport of highly water-insoluble materials through the aqueous phase is required, a collision-based transport mechanism is proposed as an alternative to the conventional diffusion-based mechanism. Examples of this approach applied to water-insoluble inhibitors,^[18,20] catalytic chain transfer agents^[19] and monomers^[6,18,21,24] have, to certain extent, been accepted by the scientific community.

Rodriguez and coworkers^[18] reported that 2,5 di-tert-butyl hydroquinone, a relatively water-insoluble inhibitor, previously dissolved in miniemulsion droplets of styrene and methyl methacrylate was capable of inhibiting the polymerization within seed polymer particles that contained oil-soluble initiator azobisisobutyronitrile, indicating that transport of the inhibitor from the miniemulsion droplets to the polymer particles took place. The authors concluded that mass transfer between the miniemulsion droplets and the seed particles took place by both collisions and diffusion in parallel, and that the higher the hydrophobicity of the species involved was, the higher the influence of the collision-based transfer would be in the system. A mathematical model was later developed based on these data by Asua et al.^[20], through which they determined that at low stirring rates of 30 rpm,

approximately two thirds of the inhibitor was transferred by diffusion and the rest by collisions, while at higher stirring rates (120 rpm) the fraction of inhibitor transferred by diffusion was reduced to only one fifth.

More recently, Jansen et al.^[6] provided experimental evidence of transport through the aqueous phase by collisions of water-insoluble monomer droplets by preparing several miniemulsions independently and later blending and polymerizing them in a single reactor. Through monitoring of the polymer thermal transitions by DSC, it was possible to identify that whether the monomers were miniemulsified separately or in a mixture, a single copolymer would be obtained, for both conventional and superhydrophobic monomers. When the authors separated the miniemulsions with a semi-permeable membrane, they found that while miniemulsions made up of conventional monomers were able to interact with one another, miniemulsions of superhydrophobic monomers could not, indicating that a significant fraction of the mass transfer of highly water-insoluble materials took place by collisions.

Additional evidence of this idea can be found in the work of Smeets et al.^[19] on the use of very hydrophobic catalytic chain transfer agents (CCTA) in emulsion polymerization, by monitoring the degree of polymerization during

the emulsion polymerization of MMA in the presence of bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (COPhBF), a virtually water-insoluble CCTA, at concentrations of 0.070 - 0.160 catalyst molecules per particle. Taking into account the low concentrations of CCTA, an effective transport mechanism of this species between the polymer particles would be required in order to get a monomodal molecular weight distribution with a polydispersity of 2, characteristic of CCTP-mediated reactions.^[25] Additionally, said transport mechanism would most likely be collision-based on behalf of its hydrophobicity. The authors found that the degree of polymerization decreased continuously while monomer droplets were still present in the reactor, and then it stabilized from the moment monomer droplets disappeared, until the end of the experiment. They proposed that the CCTA would be transported by collisions, at first between the shrinking micron-sized monomer droplets and the polymer particles, and once monomer droplets had disappeared, exclusively between the polymer particles. It could also be argued that the decreasing value of the degree of polymerization associated to the gradual collision-based transport of the CCTA to the polymerization loci, the polymer particles, would be due to the limited number of monomer droplets in the system and the increasing number of polymer particles; and that once the polymer particles became the only organic phase that remained

in the reactor, whose number was at least three orders of magnitude higher than that of the droplets, an effective collision-based transport was able to be established.

It is clear that transport by collisions is not only possible, but rather common when hydrophobic species are involved. Taking into account that most of the research conducted on the subject has been done in miniemulsion systems, a high number of monomer droplets seems to be a requirement in order to sustain viable polymerization rates. It is unlikely that the results obtained by Smeets et al.^[19], for the transport of very low concentrations of a water-insoluble CCTA in emulsion polymerization, could be extrapolated to the higher demands of an organic phase containing mostly superhydrophobic monomers, particularly during the early stages of the polymerization. However, these findings illustrate the benefits of a high number of colliding species, either monomer droplets or polymer particles, in a collision-based transport mechanism.

The ability of the hydrophobic emulsifier, Aerosol TR-70, to effectively stabilize nano-sized monomer droplets satisfies the requirement of providing an elevated number of colliding species, and hence supports the hypothesis

of an effective monomer transport based mainly on collisions in the polymerizations carried out in this chapter. In summary, the continuous presence of these monomer droplets could potentially lead to the following events within the polymerization reactor:

- Monomer droplets could transfer monomer to the existing polymer particles through collisions. Upon a collision event, the monomer of a droplet could be transferred to a particle. In the presence of radicals, polymerization of the monomer now within the polymer particles would ensue, resulting in their continuous growth.
- In account of their elevated number and consequently high surface area, monomer droplets could be able to capture radicals from the aqueous phase and nucleate, leading to new particle populations.
- Monomer mixtures containing less-than-superhydrophobic monomers could experience selective diffusion of said monomers through the aqueous phase, resulting in a polymer composition profile among the particles of the final latex. These monomers could also participate in micellar and/or homogeneous nucleation.

The likelihood of each event taking place would, in principle, depend on a variety of process conditions, particularly the number of colliding species, as it will be discussed below.

2.6.3. EFFECT OF THE NUMBER OF COLLIDING SPECIES

The colliding species in the context of this thesis are the TR-70 stabilized monomer droplets and the polymer particles. The number of monomer droplets would depend on a plethora of factors to different extents. The concentration of TR-70 emulsifier would be, in principle, among the most important; however, the relative concentrations of the other emulsifiers, as well as the concentration and nature of the monomer mixture could also play a major part. An effect would also be expected from the reaction temperature and stirring rate. The combination of all these factors certainly makes it difficult to achieve a reliable control of the total amount of monomer droplets present in the reactor. Nonetheless, the control of the number of polymer particles by adjusting the amount of seed polymer is far simpler, more reliable and easier to monitor. The results obtained for the copolymerization of LMA/IBA are proof of that, where the number of initial seed particles has shown to be a significant factor affecting the final particle size distribution of a

latex containing large amounts of superhydrophobic monomers. With this data, it is possible to pursue a more detailed interpretation of the role of the colliding species in this kind of polymerizations.

A summarized analysis of the evolution of the number of particles for the LMA/IBA copolymerizations is reported in Figure II - 15. As it was previously mentioned, reactions IBA-115-H and IBA-66-H, both with the higher number of seed particles, maintained a relatively constant value throughout the polymerization; while the remaining reactions, with lower starting number of particles, saw an increase on this variable until it eventually stabilized.

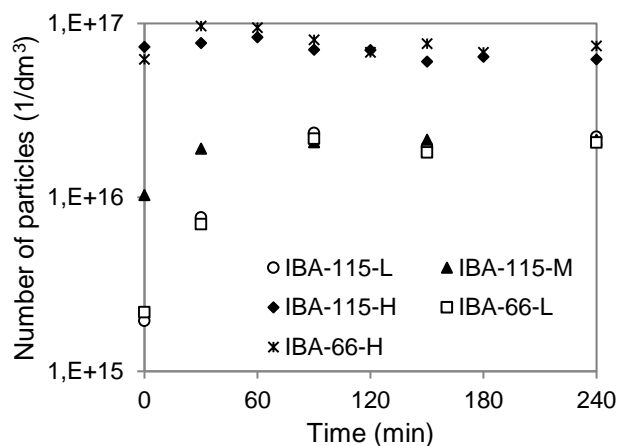


Figure II - 15. Number of particles time-evolution for the LMA/IBA copolymerizations

In the case of reactions IBA-115-H and IBA-66-H, monomer droplets at any given time in the reactor encounter a large number of particles, which were potential collision candidates. The frequency of the collisions would be high enough to allow all the monomer mass to be evenly distributed among the existing polymer particles, resulting in a narrow particle size distribution. New nucleations would be less likely to take place in this system, since both micellar and homogeneous nucleation would be severely limited by the hydrophobicity of the monomer mixture.

Reactions IBA-115-L and IBA-66-L would be placed on the other end of the spectrum. In this case, the number of colliding species was significantly lower and consequently the frequency of effective collisions, hindering the ability of the monomer to distribute itself among existing particles. The likelihood of monomer droplets capturing radicals and nucleating would be high, if their small size and relatively high stability is considered, which would result in a new particle population. After sufficient droplet nucleation events, enough particles would have been created in order to support an effective collision-based monomer transfer mechanism, and hence the total number of particles would reach a constant value.

It should be noted that the increase in the number of particles eventually reached a quite similar value before stabilizing. Interestingly, this behavior was also observed for reaction IBA-115-M which had an intermediate number of particles but still stabilized at a similar value, although earlier, in the polymerization. These findings suggest that, for any given set of conditions, such as recipe, reaction temperature and stirring rate, the number of colliding species required to support a collision-based monomer transport mechanism is rather constant. For these set of LMA/IBA polymerizations, that value was roughly $2.1 \times 10^{16} \text{ dm}^{-3}$.

The results from the DSC analyses for these two model reactions are presented in Figure II - 16. A single glass transition at around 24°C can be observed for IBA-66-H, while two broad glass transitions at -15°C and 30°C are evident for the copolymer obtained from reaction IBA-66-L. Based on these findings, it seems evident that polymerizations with a higher number of seed particles lead to a more homogenous distribution of the monomers among all the particles and, consequently, to a homogenous copolymer composition represented by a single T_g .

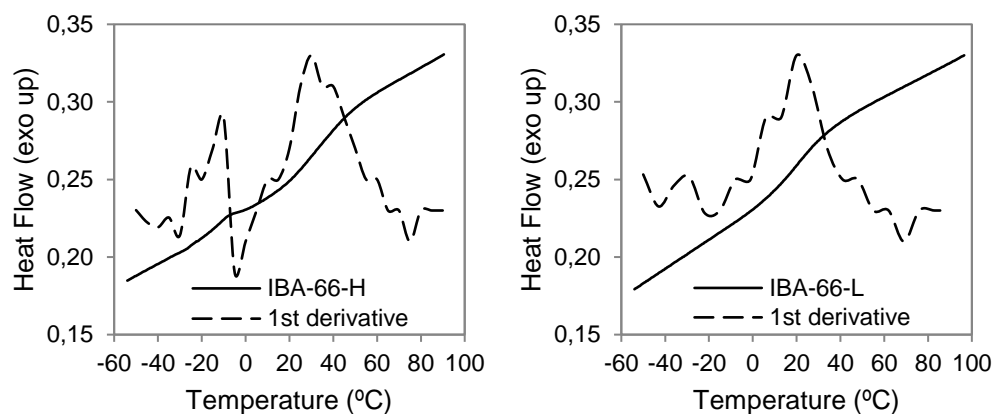


Figure II - 16. DSC Thermograms of the LMA/IBA copolymers obtained from reactions IBA-66-L (left) and IBA-66-H (right)

Furthermore, employing the Fox equation, the transitions obtained from reaction IBA-66-L would theoretically correspond to two random LMA/IBA copolymers at weight ratios of 68/32 and 32/68, for the T_g at -15 °C and 30 °C, respectively. However, it is also important to mention that the same equation estimates the T_g of a copolymer with a 50/50 weight ratio to be 6 °C, instead of the 24 °C obtained experimentally for reaction IBA-66-H. The magnitude of the increase in heterogeneity, evidenced by multiple glass transitions, cannot be explained in terms of lower conversions during the polymerizations with lower number of particles (Figure II - 8), particularly considering that both monomers seemed to polymerize at a similar rate even in such conditions (Figure II - 6). Alternatively, It seems to indicate that when collisions are not frequent enough to effectively distribute monomer among

particles, the longer residence time of the monomer droplets results in the selective transport of some monomers towards the polymer particles. Should droplet nucleation be the only event taking place in these conditions, the final copolymer composition would also be homogeneous.

While both IBA and LMA are regarded as superhydrophobic monomers in the context on this work, the water solubility of IBA is at least one order of magnitude higher than that of LMA.^[5] It has also been reported to polymerize in emulsion polymerization using conventional raw materials,^[21] as shown as well in the synthesis of multiple polymer seeds throughout this chapter. Taking these factors into account, it is possible that IBA could undergo diffusion to polymer particles while isolating LMA-rich monomer droplets, resulting in the formation of multiple random copolymers segregated among multiple polymer particles.

2.7. OPTIMIZATION OF EMULSIFIER CONTENT

The LMA/IBA copolymers discussed in the previous section were synthesized under nearly identical recipes with the exception of the variable of interest, i.e. the number of seed particles. The predominant effect of this variable, however, resulted in significant changes of the total surface area of the final

dispersions, despite all of these experiments being carried out with similar emulsifier concentrations and solids contents. Consequently, a proportional fraction of emulsifier would have been used in excess on the lower surface area polymerizations when compared to their higher surface area counterparts. This gap leaves room for further optimization of the emulsifier content in an attempt to minimize the total amount of hydrophilic species in the final dispersions while maintaining colloidal stability, and will be the main focus of this section.

Semi-batch emulsion copolymerization was utilized to prepare a series of polymer latexes. The recipe and strategy reported in Table II - 10 was implemented with the following changes: i) methacrylic acid was added to the monomer mixture, to give a LMA/IBA/MAA weight ratio of 47/50/3; ii) the amount of seed polymer was used to control the number of particles, and hence to target the total surface area to be generated during the polymerization, and; iii) the total emulsifier content was adjusted according to the estimated total surface area of the final latex. A summary of all the LMA/IBA/MAA copolymerizations performed are presented in Table II - 14.

Table II - 14. Optimization of emulsifier content in synthesis of LMA/IBA/MAA copolymer by emulsion polymerization

Reaction	Seed content*	$N_{P,Seed}$ (dm^{-3})	Estimated Area (m^2/dm^3)	Emulsifier content*
OEC-0	0.00 wt%	-----	-----	1.00 wt%
OEC-5	0.05 wt%	1.8×10^{15}	3317	0.70 wt%
OEC-10	0.10 wt%	5.0×10^{15}	4178	0.90 wt%
OEC-50	0.50 wt%	3.2×10^{16}	7240	1.50 wt%
OEC-260	2.60 wt%	1.2×10^{17}	12218	2.50 wt%

*: Based on monomers

Methacrylic acid was included to improve the wetting of the latexes over hydrophilic substrates, such as glass, and also to open a door for future surface chemistry.^[10] The estimation of the total surface area of the final latex was done under the assumption that there would be no secondary nucleations during the experiment, and that monomers would be distributed homogeneously among the existing polymer particles. While the total emulsifier content used was variable, their relative ratios were kept constant and equal to the values reported in Table II - 10 (TR70/A102/SLS: 1.0/2.0/1.5 in weight basis).

The total emulsifier content for each reaction was calculated assuming a surface coverage value of 25%, which is said to provide close to 70% of the surface potential of a stabilizing monolayer;^[26] to that end, titration of a diluted poly(LMA/IBA) dispersion with a TR70/A102/SLS emulsifier mixture solution was carried out while monitoring surface tension following the procedure described in section 2.2.3, in order to determine the corresponding parking area. Both the monomer ratio of the latex and the emulsifier ratio of the mixture were similar to those implemented in the polymerizations. Previous to the titration of the diluted latex, it was cleaned in dialysis tubes (Spectra/Por®, MWCO:12-14,000) for a prolonged period of time to remove existing surfactant and other hydrophilic species.

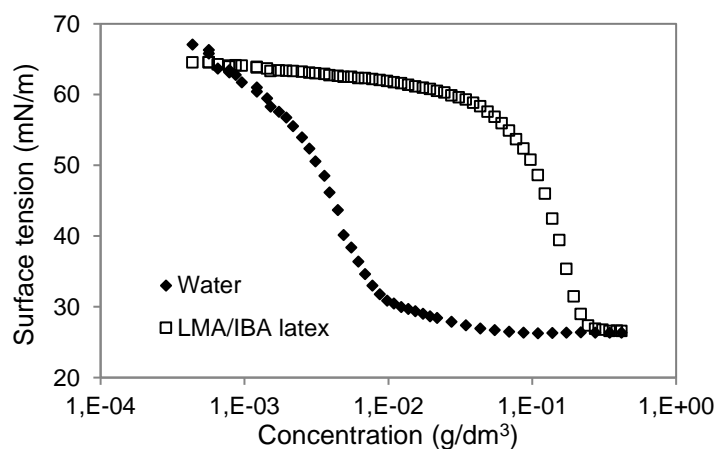


Figure II - 17. Surface tension vs. emulsifier concentration of the TR70/A102/SLS mixture with and without poly(LMA/IBA) particles

The results obtained for the titration of the emulsifier mixture, both in absence and in the presence of polymer particles, are presented in Figure II - 17. The change in the slope during the titration in water was found at a concentration of $9.80 \times 10^{-3} \text{ g/dm}^3$, which is essentially the critical micelle concentration of the mixture of emulsifiers. The change of slope in the experiment carried out in the diluted latex was found at a much higher concentration, $2.97 \times 10^{-1} \text{ g/dm}^3$, since the emulsifier must first saturate the available polymer surface before forming micelles. Inputting these values in (Equation II - 5), the parking area was determined to be approximately $300 \text{ m}^2/\text{g}$.

A new polymer seed was synthesized for this series of polymerizations, using a modified version of the recipe reported in Table II - 11 with an A-102 emulsifier content of 3.33 wt% based on monomers. Instead of homopolymerizing IBA, a monomer mixture of IBA/BA at a 70/30 weight ratio was used in order to further decrease the particle size. The remaining steps of the recipe were carried out identically. High conversions were measured gravimetrically and the average particle size of the IBA/BA seed determined by DLS was 53 nm, with a \mathcal{D} value of 0.032.

The issue of colloidal stability of the latexes obtained by semi-batch emulsion polymerization of this seed is addressed in Figure II - 18, where the coagulum content is plotted together with the emulsifier surface coverage.

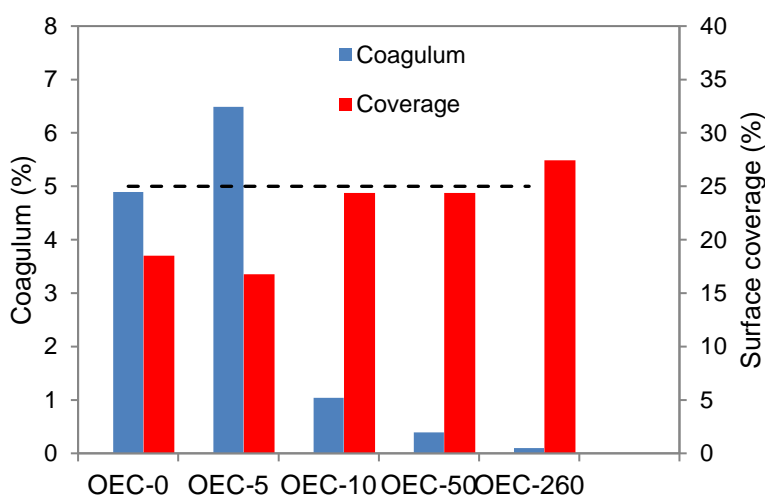


Figure II - 18. Coagulum content vs. emulsifier surface coverage of the LMA/IBA/MAA polymer particles

At first glance, it can be observed that polymerizations OEC-10, OEC-50 and OEC-260 had the highest surface coverages and also the lowest coagulum contents. Additionally, the surface coverage values were quite close of the targeted 25% of the recipe, suggesting that both the total surface area and the corresponding emulsifier estimation were adequate. On the other hand, polymerizations OEC-0 and OEC-5 resulted in elevated coagulum contents as well as surface coverage values well below the desired 25%.

The main difference between these two cases was the ability to adequately estimate the expected surface area, and thus the corresponding emulsifier content to account for it. As previously discussed in section 2.6.3, polymerizations with a number of particles under a given threshold are not able to effectively distribute monomer through a collision-based mechanism and hence uncontrolled nucleations take place. The PSD time-evolutions of reactions OEC-0, OEC-5, OEC-50 and OEC-260 presented in Figure II - 19 are submitted as further evidence of this claim.

Reaction OEC-5 followed a similar evolution of that of the previously discussed reaction IBA-66-L, with a similar content of seed polymer and initial number of particles. On the other hand, reactions OEC-50 and OEC-260, represented additional examples of polymerizations with a number of seed particles high enough to support an effective collision-based monomer transport mechanism, where a theoretical progression of the particle size without secondary nucleations took place. In both cases, the polydispersity of the particle size distribution was largely preserved.

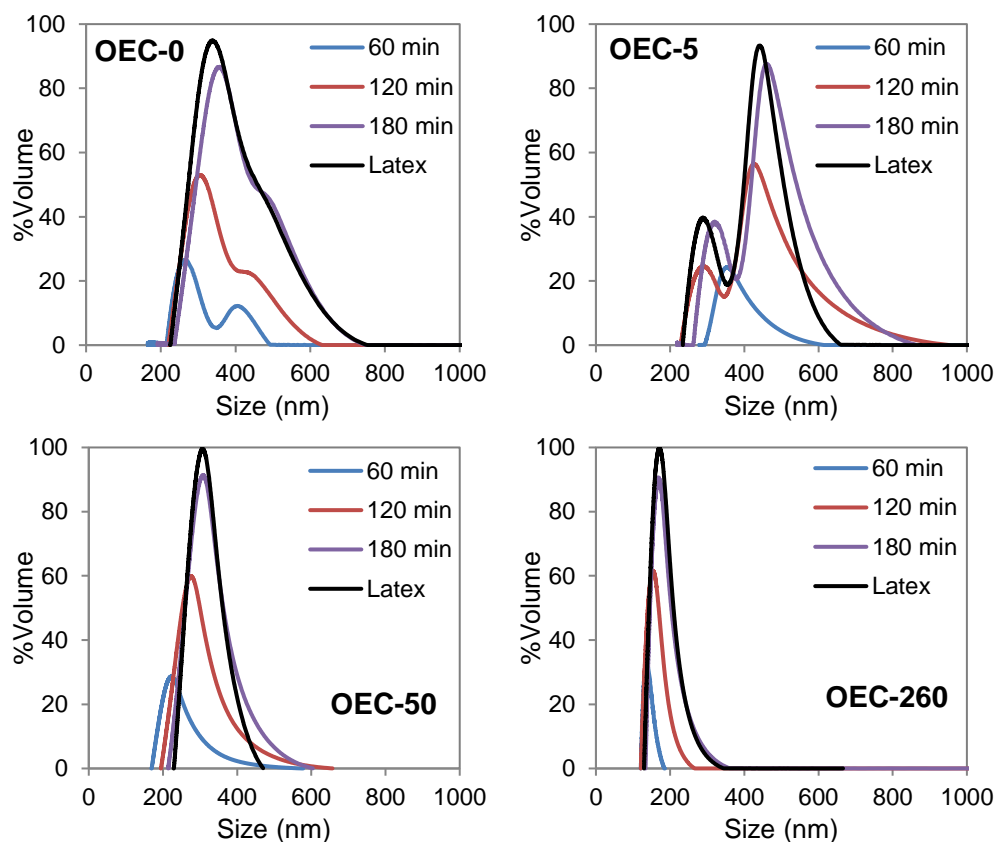


Figure II - 19. PSD time-evolutions of the LMA/IBA/MAA copolymerizations J

From these observations, it can be concluded that despite the differences in the monomer transport mechanisms involved when polymerizing superhydrophobic monomers through this technique, colloidal stability is a surface related issue in a similar way to a conventional emulsion polymerization. That said, keeping track of the surface area generated during a reaction is of utmost importance if colloidal stability is to be preserved.

2.8. CONCLUSIONS

The polymerization of superhydrophobic monomers in aqueous media was investigated through emulsifier combination in emulsion polymerization, a new technique initially based on an amalgamation of literature results that pointed towards the use of hydrophobic surfactants as a key element to successfully achieve said objective. Emulsion homopolymerization and copolymerization of lauryl methacrylate, with either conventional monomers like butyl acrylate and methyl methacrylate, or another superhydrophobic monomer called isobornyl acrylate, were carried out successfully at solids content as high as 40%. The effects of several initiation systems, as well multiple emulsifiers in combination were studied. Batch and semi-batch feeding strategies; both in the presence or absence of polymer seed particles, were implemented. These efforts were made in order to gain insight regarding the mechanism involved in these polymerizations, and to possibly establish a framework within which this and other monomer systems could be successfully polymerized.

Attempts at the homopolymerization of LMA in a batch system, both with conventional and hydrophobic emulsifiers, led to either low conversions or high coagulum contents. Additionally, using an oil-soluble initiator produced

low molecular weight polymer, suggesting the experiment took place in a non-compartmentalized system.

Homopolymerization in a semi-batch system including a hydrophobic emulsifier produced molecular weights in the same order of magnitude as those obtained in miniemulsion polymerization, although the latex obtained was not colloidally stable. However, it was possible to significantly improve the colloidal stability of the latexes by making the nature of the polymer phase more hydrophilic, and consequently increasing the parking area of the emulsifiers, through copolymerization of LMA with either conventional monomers or IBA, while maintaining high level of superhydrophobic monomer incorporation. Additionally, the number of initial seed particles was shown to be the main determining factor of the kinetics, particle size distribution, polymer composition, and colloidal stability of the latexes produced.

The success of these copolymerizations was attributed to the presence of emulsifier Aerosol TR-70 and its ability to stabilize nano-sized monomer droplets in water. The presence of these droplets satisfied the requirement of providing an elevated number of colliding species to support a collision-based monomer transport mechanism. During the polymerizations, the following

events would take place to varying extents depending on the recipe and the process conditions:

- Monomer droplets would transfer monomer to the existing polymer particles through collisions. In the presence of radicals, polymerization of the monomer now within the polymer particles would ensue, resulting in their continuous growth.
- In account of their elevated number and consequently high surface area, monomer droplets could be able to capture radicals from the aqueous phase and nucleate, leading to new particle populations.
- Monomer mixtures containing less-than-superhydrophobic monomers could experience selective diffusion of said monomers through the aqueous phase, resulting in a polymer composition profile among the particles of the final latex.

Despite the differences in the monomer transport mechanisms involved when polymerizing superhydrophobic monomers, colloidal stability was confirmed to be a surface related issue in a similar way to a conventional emulsion polymerization.

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Chapter III. MINIEMULSIFICATION BY PHASE INVERSION TEMPERATURE

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3.1. INTRODUCTION

Phase inversion processes have provided a way to prepare kinetically-stable emulsions of very small size that have seen applications geared towards several fields, such as the food,^[1] pharmaceutical,^[2] cosmetics^[3,4] and petroleum industries,^[5,6] as reviewed by Salager et al.^[7], Tadros et al.^[8] and more recently by Perazzo et al.^[9] The advantages of the resulting emulsions are usually associated to their outstanding colloidal stability and optical transparency. Colloidal stability is understood to be a consequence of the tiny droplet radius and its maximization of steric repulsion through the reduction of configurational entropy, and its hindering of the sedimentation velocity and eventual phase separation of the droplets;^[10] while optical transparency is also associated to small droplet radii and their reduced capacity to scatter light waves, generally resulting in nearly transparent emulsions. Since both properties are directly related to their small size, they have been usually called nanoemulsions; although less frequently the term miniemulsion has also been utilized when polymerization is meant to follow. In this thesis and throughout this chapter, the process will be generally referred to as “miniemulsification by phase inversion”, as opposed to the classical

miniemulsification process involving high energy mixing, and the final product will continue to be called a “miniemulsion”.

Miniemulsification by phase inversion, as the name indicates, relies on the inversion between the continuous and dispersed phase that is achieved either by changing a formulation variable, such as pH, temperature or surfactant ratio, or by changing composition. The result of both processes is a finely dispersed emulsion, but the methods involved present several key differences. For example, when a formulation variable is used to trigger the inversion, the process is reversible, which resulted in this phase inversion method being referred to “transitional phase inversion”. On the other hand, when a composition variable is used instead the inversion process is irreversible, in what is typically referred to as “catastrophic phase inversion”.^[7]

In some fields the miniemulsions prepared by phase inversion are formulated by adding a series of components, such as defoamers, thickeners and inorganic fillers, but it is rather uncommon for them to participate in chemical reactions. Applications of phase inversion processes in polymerization are far less common, most of them focusing on secondary dispersion of

polycondensates;^[11-13] however, as reviewed in Chapter I of this thesis, a few examples can be found in literature.^[14-22]

Spernath and Magdassi^[14] successfully prepared and polymerized a miniemulsion of lauryl acrylate through transitional phase inversion, where temperature was the control variable. Fast cooling to room temperature of an emulsion previously taken past its phase inversion point, which was determined by the nature and concentration of a mixture of alkyl polyglycoethers as emulsifiers, allowed the preparation of the miniemulsion. Galindo-Alvarez et al.^[16] implemented the alternative Near-PIT method, where the initial emulsion is not heated past its inversion point but a few degrees short, to prepare styrene miniemulsion using similar emulsifiers and hexadecane as costabilizer. Sadtler and coworkers^[17] were also able to prepare similar styrene miniemulsions but employing catastrophic phase inversion instead. In all these three cases, a monomer content of approximately 20 wt% and overall emulsifier content in the vicinity of 5 wt% was employed.

The limited number of applications of these methods in miniemulsion polymerization has been associated to either the demanding emulsifier

requirements in transitional phase inversion, or the elevated droplet sizes typically obtained through catastrophic phase inversion.^[23] The work of Sadtler et al.^[17] could be considered an exception to the latter comment since tiny droplet sizes were obtained; however, as the authors pointed out, a Winsor III type emulsion was necessary in order to reach such droplet sizes and it was only through elevated emulsifier contents that said emulsion morphology was obtained. In another work, Sajjadi^[24] studied the nature of the inversion in a model cyclohexane-surfactant-water system, reporting that an emulsion can undergo transitional phase inversion and achieve nanoscale droplet sizes only if enough emulsifier was available to stabilize a bicontinuous microemulsion phase, and in cases where the emulsifier content was lower than that the inversion mechanism would shift from transitional to catastrophic, leading to the formation of larger micron-sized droplets. Based on these results, it is possible that a monomer emulsion relying only on catastrophic phase inversion cannot reach droplet sizes low enough to be polymerized by droplet nucleation and yield commercially attractive polymer latexes, leaving only transitional phase inversion as a viable alternative for this purpose.

Regardless of the elevated surfactant contents, transitional phase inversion has provided a viable method to prepare miniemulsions of hydrophobic organic phases, including the so-called superhydrophobic monomers that are the main focus of the present thesis. Therefore, this method will be implemented throughout this chapter where temperature will be the formulation variable selected to trigger the inversion of the organic and aqueous phases, and will be referred to as phase inversion temperature (PIT). Emulsifiers will be selected based both on previous experimental results obtained for similar systems and fundamental knowledge derived from them, available in the open literature. The effect of relevant variables of a typical transitional phase inversion system, such as the nature and quantity of the emulsifiers used on the colloidal stability of the emulsion and on the inversion temperature will be investigated, and general guidelines of the use of this low-energy miniemulsification technique in the batch polymerization of superhydrophobic monomers will be described.

3.2. EXPERIMENTAL

3.2.1. MATERIALS

The monomers lauryl methacrylate (LMA, 96 wt% rest on isomers, Sigma-Aldrich) and isobornyl acrylate (IBA, technical grade, Sigma-Aldrich) were used as supplied without any additional purification steps. All the emulsifiers used in this chapter were non-ionic ethoxylates and their descriptions and corresponding hydrophilic-lipophilic balance (HLB) values are reported in **Table III - 1**. Batch miniemulsion polymerizations were initiated by a redox system consisting of several pairings of oxidant t-butyl hydroperoxide (TBH, 70% solution in water from Sigma-Aldrich) and reductants ascorbic acid (ASA, 99% ACROS) and sodium formaldehyde sulfoxylate (SFS, 99% Fluka). Sodium chloride (NaCl, >99.5% Sigma-Aldrich) was added to the aqueous phase during the miniemulsification process. Hydroquinone (99%, Panreac) was used for stopping the polymerization in the samples withdrawn from the reactor, and double deionized water (MilliQ standards) was used in all the experiments.

Table III - 1. List of emulsifiers used and their relevant characteristics

Emulsifier	Description	Moles EO	HLB*	Provider
Triton X-100	Octylphenol	9.5	13.4	Dow
Brij S2	Stearyl ether	2	4.9	Uniquema
Brij O10	Oleyl ether	10	12.4	Uniquema
Brij O20	Oleyl ether	20	15	Uniquema

*: Provided by the manufacturer technical specification sheets

3.2.2. MINIEMULSIFICATION BY PIT

Monomer miniemulsions were prepared in a small 200 mL jacketed glass reactor fitted with a low-energy magnetic stirrer, as well as with a temperature and electrical conductivity probe (Crison micro CM2201). An external water bath with a heating power of 2.6 kW (Lauda ECO Gold) was connected to the reactor's jacket and was used to adjust the emulsion temperature. A viscous silicone was applied to the reactor connections to provide sealing during the experiments.

A typical phase inversion temperature procedure was followed. Initially, a coarse oil in water (o/w) emulsion consisting of water, monomers and emulsifier was prepared under continuous low-energy agitation applied with a magnetic bar. Taking into account that the conductivity measured for a normal emulsion under agitation is that of the continuous phase, this variable is

commonly used to detect the moment at which phase inversion takes place.^[25] To that end, a small amount of NaCl was also added to the aqueous phase to provide enough electrical conductivity to facilitate the identification of phase inversion temperature without affecting the phase distribution behavior of the emulsion. The emulsion was heated until a sharp decrease down to zero conductivity was observed (characteristic of the oil phase), and the inversion temperature was registered. The now water in oil (w/o) emulsion was cooled as quickly as the experimental setup would allow through the addition of ice into the external bath, returning to an o/w morphology. In occasions, several heating and cooling cycles were also performed on the same emulsion while monitoring the inversion temperatures. The temperature range covered in these experiments went from 30 °C up to 90 °C, due to the evaporation of water at atmospheric conditions at 100 °C and foreseeing that this process would not be scaled up to pressured reactors in this work. The cooling rate was found to be approximately 20 °C/min between 90 and 60 °C, and later just under 10 °C/min, although an automated control system was not put in place to control and monitor this variable. A general recipe detailing the relevant variables and ranges covered in the PIT experiments throughout this chapter is reported in **Table II - 4**.

Table III - 2. Miniemulsion preparation through the PIT method

Variable	Value
Monomer content	17 – 44 wt%
Emulsifier content	2.5 – 7 wt%
Temperature range	30 – 90 °C
Stirring rate	200 rpm
Salinity	10 mM NaCl

3.2.3. POLYMERIZATION OF THE MINIEMULSIONS

Batch polymerization of the miniemulsions prepared by PIT was carried out on the Mutiplant M100 system (Chemspeed) described in the previous chapter. The miniemulsions were transferred to 80 mL metallic reactors and purged with nitrogen during 10 minutes, before they were heated to 60 °C, the polymerization temperature unless stated otherwise. Aqueous solutions of TBH and ASA were fed in parallel over a period of 60 minutes after which the reactor was kept at the reaction temperature for additional 30 minutes, before cooling down to room temperature and filtering the resulting latex with a filter with a pore size of 80 µm. The total TBH content fed was equivalent to 1 wt% based on monomers, while the total amount ASA corresponded to a 2.0 TBH/ASA mole ratio. Samples were regularly withdrawn from the reactor and

stabilized with a few drops of a 1 wt% hydroquinone solution, in order to analyze conversion and particle size evolution.

3.2.4. CHARACTERIZATION OF MINIEMULSIONS AND LATEXES

Monomer conversion

Monomer conversion was determined by both gravimetric and $^1\text{H-NMR}$ using the same procedure described in section 2.2.3. Since only batch polymerizations took place in this chapter, only overall monomer conversions are reported.

Average droplet and particle size

The average droplet and particle size was measured for the miniemulsions and latexes, respectively, by dynamic light scattering (DLS) at 25 °C using the apparatus and procedure also described in section 2.2.3. Volume and z-average sizes are reported throughout this chapter, as well as the PDI index (\mathcal{D}) representative of the broadness of the distributions.

Gel content & average molecular weight

Soxhlet extraction was implemented to determine gel content and to separate the soluble polymer fraction that would later undergo molecular weight measurements by gas permeation chromatography (GPC). A detailed description of the methods and equipment utilized can be found in the previous chapter.

Miniemulsion stability

The stability of the miniemulsions was determined using static multiple light scattering in a Turbiscan Lab Expert apparatus (Formulaction). The equipment performed backscattering measurements at an angle of 135° from the incident beam using a pulsed near IR light source at a wavelength of 880 nm, along the height of a vial containing the miniemulsions. Scans were taken every 40 μm over a total length of 55 mm. A 25 mL vial was filled with approximately 20 mL of the miniemulsions shortly after they were prepared, and scanned every 10 minutes for a period of 1 to 12 hours, at either 30 $^\circ\text{C}$ or 60 $^\circ\text{C}$. Multiple scans are made along the height of the vial in order to obtain a comprehensive plot of the backscattering profile. A comparative analysis of these profiles over time allows the discernment of colloidal instability events

that could be taking place in the samples, such as droplet migration or droplet coalescence.

3.3. EMULSIFIER SELECTION

The choice of emulsifier is certainly one of the most influential decisions to be made in a colloidal system. Not only must the emulsifier be capable of providing colloidal stability to the emulsion, but if polymerization is involved, it must also be able to do that during and long after the polymerization process is finished. In a phase inversion temperature system additional requirements must be considered as well, such as high sensitivity to temperature changes in the range selected to trigger the inversion. For this method to be viable in emulsion polymerization, the inversion temperature should be between 60 and 90 °C; the upper limit being established by the boiling point of the continuous phase while the lower limit being set by reaction temperature, which must be lower than the PIT.

Several approaches can be taken in order to make a proper selection, such as a theory-guided methodology based on the characteristics of the emulsifiers themselves and the organic phase of interest through the

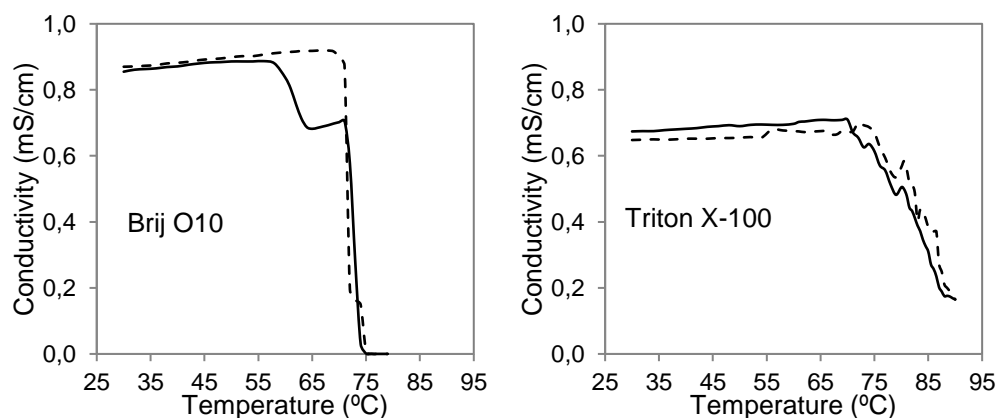
application of the HLD theory described in Chapter I.^[26] This is often combined with the use of phase diagrams describing the behavior of the emulsion at different concentrations of the emulsifiers and the ratio between the aqueous and organic phases, effectively accounting for both formulation and composition variables simultaneously. Examples of the use of ternary phase and surfactant fish diagrams, as well as other two-dimensional and three-dimensional representations of phase behavior, can be found in extensive detail in the open literature.^[27-31]

This approach, while comprehensive and detailed, can also be time consuming as phase diagrams must be developed for combinations of multiple formulation variables in order to be effective. Additionally, in a polymerization system where monomer selection is often dependent on other performance-related variables that often require adjustments, developing phase diagrams might not be a viable option. Taking this into consideration, an empirical approach towards the optimization of emulsifier selection and concentration was implemented in the present work, based on previous results found in the literature for similar systems and a limited application of the HLD method.^[26,32]

Several authors^[14-18,20] have obtained positive results preparing polymerizable miniemulsions of several monomers in PIT systems by using $C_{18}EO_j$ alkyl polyglycoethers emulsifiers, i.e. a polyethoxylated stearyl/oleyl hydrocarbon chain where the j is number ethylene oxide moles of the hydrophilic section. Utilizing the HLD equation (Equation I - 1) by substituting approximate values provided by Salager et al.^[26] for these emulsifiers and LMA as the organic phase, confirmed that emulsifiers with 9 to 11 moles of ethylene oxide would result in emulsions with phase inversion temperatures between 60 and 93 °C. For comparative purposes, a similar calculation was done with the parameters corresponding to another common emulsifier type used in PIT experiments,^[18,24] alkylphenol ethoxylates of the form C_8PhEO_j , resulting in inversion temperatures between 88 to 121 °C for the same number of ethylene oxide moles (subscript j). The parameters and results obtained are presented in **Table II - 3**. It is worth mentioning that the values for the parameter α characteristic of the hydrophobic tail of $C_{18}EO_j$ emulsifiers, as well as the *EACN* of LMA, were not readily available in reference^[26] and closest estimates were taken instead. The parameter α was extrapolated in the same fashion implemented by Acosta,^[32] while the *EACN* of LMA was taken from ethyl oleate, the only ester found in reference.^[26]

Table III - 3. Values of the parameters of the HLD equation

Parameter	Value	
Emulsifier	C ₁₈ EO _j	iC ₈ PhEO _j
α	7.9	6.2
b	0.13	0.13
k	0.15	0.15
$EACN$	6.5	6.5
t	0.06	0.06
EON	9 – 11	9 – 11
T	60 – 93 °C	88 – 121 °C


Figure III - 1. Conductivity vs temperature profiles of a 20 wt% LMA emulsion using 7 wt% of Brij O10 (left) and Triton X-100 (right)

An initial attempt at preparing miniemulsions of LMA using these two types of emulsifiers was carried out, utilizing Brij O10 and Triton X-100 as representative candidates separately. The total LMA and emulsifier contents were 20 and 7 wt%, respectively, and the conductivity vs temperature profiles

for both the heating (solid lines) and cooling (dashed lines) cycles are presented in **Figure III - 1**. A sharp decrease in the electrical conductivity was detected in both cases, although only the emulsion prepared with Brij O10 reached zero conductivity, while the one prepared with Triton X-100 did not. A reasonable degree of overlapping of the heating and cooling cycles was evidenced in both experiments, suggesting the process was reversible as expected in transitional phase inversion. Additionally, the inversion temperature of 75 °C measured for Brij O10 closely matched the one estimated by the HLD equation of 76 °C, at the conditions studied. It is highly likely that the Triton X-100 required slightly higher temperatures to reach a complete phase inversion, as estimated by the HLD equation (96 °C); however, these conditions would rest outside the adequate range of miniemulsification at atmospheric conditions.

Relevant information can also be derived from the shape of the conductivity vs. temperature profiles of both emulsions. In the case of the Brij O10 emulsion, the initial decay of conductivity to 0.68 mS/cm could be associated to the transition of the emulsion from an oil-in-water morphology (Winsor I), to a morphology containing a bicontinuous microemulsion phase (Winsor III or IV). This behavior could also be attributed to mixing, since the experiment

was conducted under lower energy intensive conditions than the ones commonly utilized.^[14,16] Additionally, the cooling cycle which involved an already prepared and homogenized miniemulsion instead of a coarse macroemulsion, did not present a discontinuity on its profile, supporting this hypothesis.

Based on these findings, Brij O10 was selected as the main emulsifier used throughout all subsequent PIT experiments.

3.4. VARIABLES AFFECTING THE PIT

As it was mentioned in the previous section, emulsifier selection plays an important role not only on the colloidal stability of the system, but also on the temperature range at which an emulsion will reach the optimal conditions to undergo phase inversion. While given the appropriate data the HLD equation could provide a quick and reliable estimate of this range, it only accounts for the effect of formulation variables. It is well known that both composition variables and the emulsification procedure itself affect not only the inversion temperature, but also determine if a phase inversion could take place in the first place.^[9,27,28] Taking that into account, the total emulsifier content and the

HLB of the emulsifier mixture utilized on the phase inversion temperature will be independently studied.

3.4.1. EFFECT OF THE TOTAL EMULSIFIER CONTENT ON THE PIT

The effect of the total emulsifier content was investigated in a range from 3 to 10 wt% of Brij O10, in miniemulsions with LMA contents of 17 and 23 wt%, and the corresponding results are presented in **Figure III - 2**.

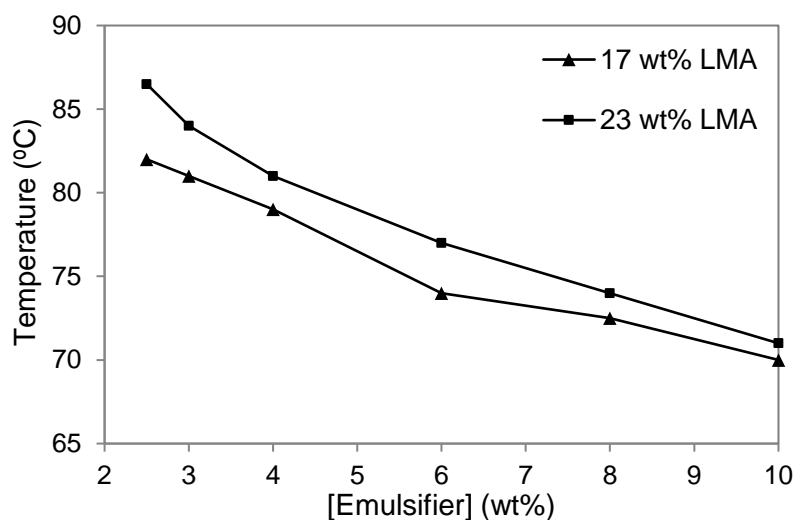


Figure III - 2. Effect of the emulsifier content on the inversion temperature

Phase inversion temperature clearly decreased as total emulsifier content increased, going from 82 and 86 °C for emulsions 17 and 23 wt% LMA,

respectively, to 70 and 71 °C in each case. Higher monomer contents also resulted in higher inversion temperatures. The results were in agreement with those reported by Spornath and Magdassi^[14] for a similar system, as well as numerous PIT systems published in open literature.^[30,33]

The droplet sizes and DLS polydispersities obtained by dynamic light scattering of the miniemulsions are reported in **Figure III - 3**. A sharp decrease on the droplet size could be observed in the range from 2.5 to 4.0 wt% and 2.5 to 6.0 wt% of emulsifier content, for the 17 wt% and 23 wt% LMA miniemulsions, respectively. Within this range, the miniemulsions also became significantly less polydisperse, and as will be observed later in this chapter, more stable.

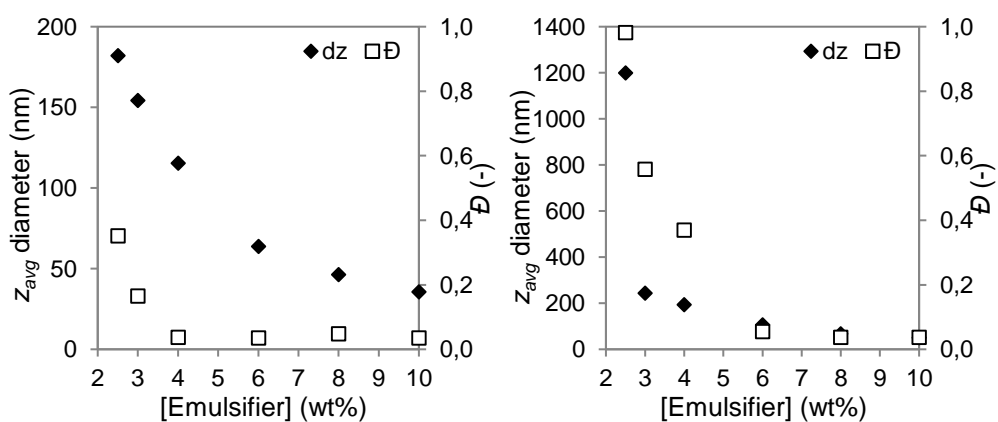


Figure III - 3. Effect of the emulsifier content on the droplet size and polydispersity of the 17 wt% (left) and 23 wt% (right) LMA miniemulsions

The sudden decrease in polydispersity was probably associated to the formation of a single phase bicontinuous microemulsion (Winsor IV) at the inversion point, once enough emulsifier was available to extend the previous middle phase of a Winsor III emulsion to the whole vessel. In other words, in emulsions with these elevated amounts of emulsifier, there are no excess organic and water phases to mechanically emulsify at the inversion point. Further increases in the emulsifier content do not significantly decrease the droplet size, as it tends to aggregate in the aqueous phase forming micelles instead of stabilizing new droplets.

3.4.2. EFFECT OF THE EMULSIFIER HLB ON THE PIT

The effect of the HLB of the emulsifier mixture on the phase inversion temperature was investigated by preparing blends of Brij S2 (HLB 4.9), Brij O10 (HLB 12.4) and Brij O20 (HLB 15) and performing PIT experiments. The HLB of Brij O10 (12.4) was used as a reference. The results obtained are reported in **Figure II - 4**. It was observed that increasing the HLB of the emulsifier mixture, i.e. adding Brij O20 to the mixture, resulted in higher inversion temperatures. The opposite was also confirmed by adding Brij S2 to the mixture.

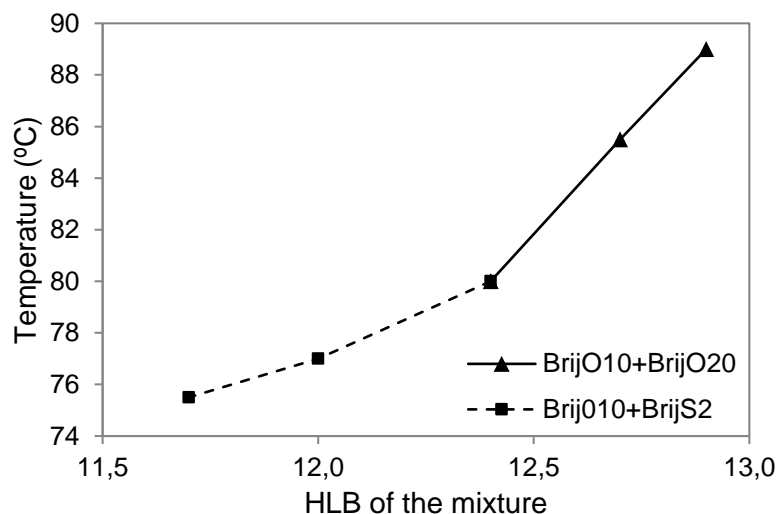


Figure III - 4. Effect of emulsifier HLB on the phase inversion temperature

The general trends of the inversion temperature were in accordance with both previously reported data,^[14,16] and the results obtained by substituting different EON values into the HLD equation (Equation I - 1); however, in order to be able to use the latter as a predictive tool it would be necessary to generate more empirical data with these type of emulsifiers.

Taking into account the information gathered thus far, it has been confirmed that adjusting emulsifier content and HLB allows the modification of the phase inversion temperature with a great degree of flexibility. These variables could be a powerful tool for the selection of an appropriate inversion temperature in the preparation of polymerizable miniemulsions, considering that it is

necessary to perform the polymerization at temperatures lower than the inversion point.

3.5. STABILITY OF THE MINIEMULSIONS PREPARED BY PIT

There are two emulsifier contents that must be satisfied in order to perform a successful miniemulsification by transitional phase inversion. The first is the bare minimum amount of emulsifier required to trigger the phase inversion, which has traditionally being associated to the quantity required to stabilize a bicontinuous microemulsion phase in a Winsor III system.^[28,31] However, not every phase inversion experiment results in a miniemulsion that is adequate for polymerization, as will be explained in this section. It is necessary that the miniemulsions are colloidally stable, after the phase inversion process and during the polymerization, in order to produce stable polymer dispersions. This secondary requirement generally calls for an additional amount of stabilizer, though it is generally desirable to keep it to a minimum.

Keeping that in mind, the objective of this section was to determine a reasonably high monomer content that could be successfully emulsified through phase inversion with the lowest amount of emulsifier. To that end, the

stability of several LMA miniemulsions prepared with Brij O10 as emulsifier was evaluated by multiple static light scattering on a Turbiscan equipment for a period of one hour after the phase inversion process had been completed. Since both droplet sizes and dispersed phase concentrations have a major influence on the scattered light, this series of scans allowed the identification of disturbances on the phase equilibrium that resulted in changes in the local concentration of the dispersed phase throughout the emulsion. The results obtained for a few limiting cases where the difference in backscattering profiles was significant are presented in **Figure III - 5**.

At the top left, the results for an emulsion whose emulsifier content was below the minimum required for transitional phase inversion to take place can be observed. Backscattering intensity quickly decreased in the bottom of the vial, while it simultaneously increased at the upper half, indicating migration of the dispersed phase towards the top (creaming) was taking place. This profile was categorically different from all the others reported in **Figure III - 5**, where phase inversion did take place, although different degrees of colloidal stability could still be noticed.

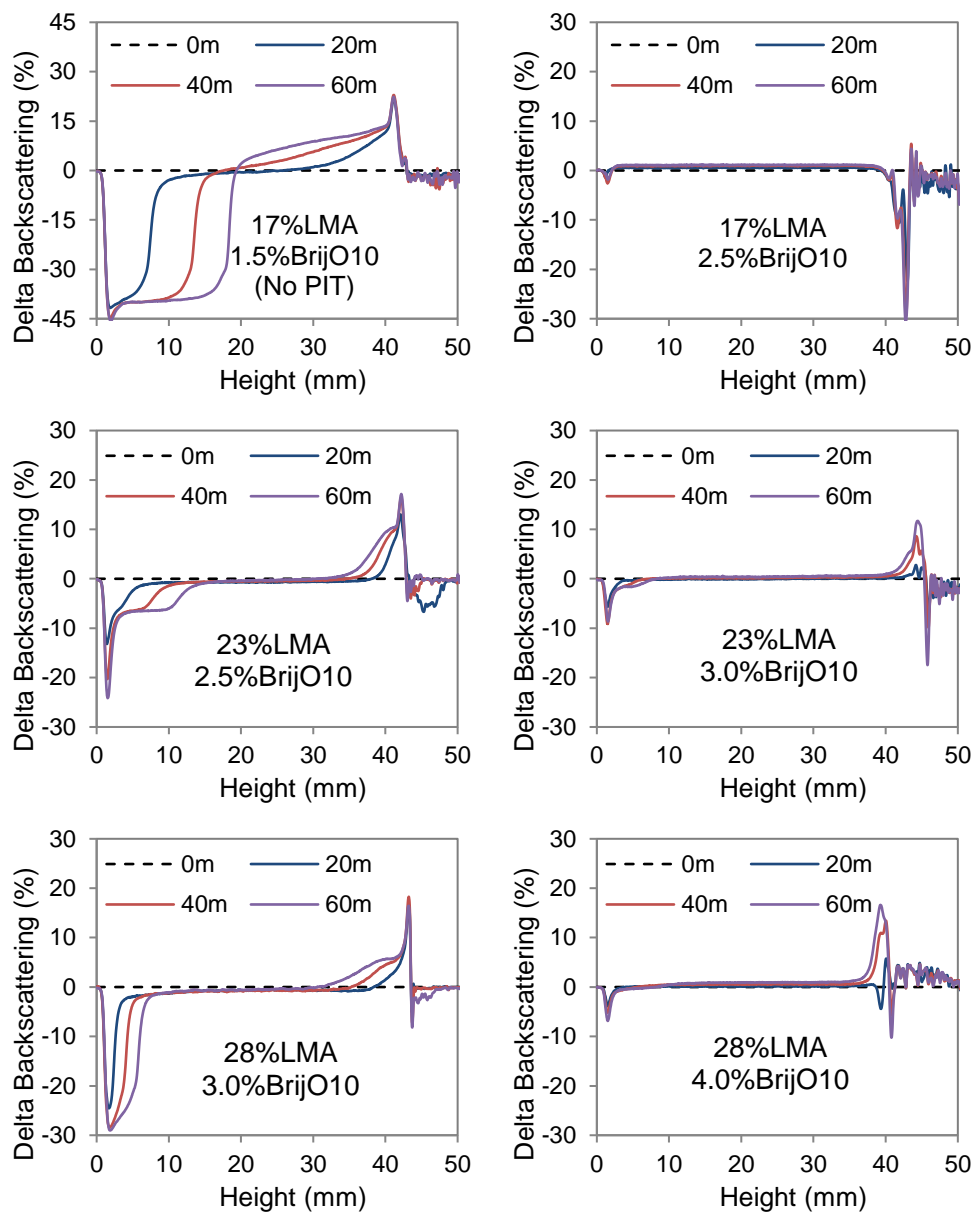


Figure III - 5. Colloidal stability analyses of relevant LMA miniemulsions

Increasing the amount of emulsifier to 2.5 wt% derived in a miniemulsion with remarkable stability, keeping a constant backscattering profile throughout the filled portion of the vial. An increment of the monomer content to 23 wt% (middle-left) lead to the loss of colloidal stability and renewal of migration events; however, this could be once again corrected by another raise of emulsifier content to 3.0 wt% (middle-right). Through several iterations of this procedure it was possible to determine the minimum emulsifier content needed to obtain stable miniemulsions at varying LMA levels, establishing a so-called boundary of colloidal stability applicable to this system, represented as a yellow line in **Table II - 10**. Miniemulsions located above this boundary were considered to be not stable enough to polymerize, including cases located on the top-right of this table, above the red line, in which the emulsions did not reach a phase inversion point in the temperature range studied. On the other hand, miniemulsions under the boundary were deemed stable enough to move on to the polymerization step. Moreover, miniemulsions located below the green line besides being remarkably stable, were also translucent.

Table III - 4. Dynamic light scattering results of the miniemulsions prepared along the boundary of stability by the phase inversion temperature

	Monomer content [LMA] (wt%)					
	17	23	28	33	38	44
2.5	d_{v1} : 140 d_{v2} : 725 \bar{D} : 0.35	d_{v1} : 113 d_{v2} : 832 \bar{D} : 0.98				No inversion
3.0		d_{v1} : 101 d_{v2} : 550 \bar{D} : 0.56	d_{v1} : 95 d_{v2} : 637 \bar{D} : 0.99			
4.0			d_{v1} : 130 d_{v2} : 454 \bar{D} : 0.38	d_{v1} : 106 d_{v2} : 678 \bar{D} : 0.51		
4.5				d_{v1} : 117 d_{v2} : 574 \bar{D} : 0.43	d_{v1} : 98 d_{v2} : 904 \bar{D} : 0.79	
5.5					d_{v1} : 106 d_{v2} : 381 \bar{D} : 0.41	d_{v1} : 176 d_{v2} : 749 \bar{D} : 0.50
7.0	Optical clarity					d_{v1} : 117 d_{v2} : 370 \bar{D} : 0.28

d_{v1} : volume-average of the small droplet population, d_{v2} : volume-average of the large droplet population, \bar{D} : PDI index

Also reported in **Table II - 10** are the results from dynamic light scattering measurements of the miniemulsions, where it could be evidenced that all the experiments conducted along the boundary of stability presented bimodal droplet size distributions. There is general consensus that the small droplets present in miniemulsions prepared by this method originate from the formation of a bicontinuous microemulsion phase at the inversion point and its

eventual disruption when the system is cooled and taken out of the inversion range.^[34] As mentioned previously on section 3.4.1, the emulsion at the inversion point could be classified as either a three-phase Winsor III microemulsion, or a single phase Winsor IV microemulsion, depending on the quantity of surfactant. In the former case, mechanical emulsification of the excess oil and aqueous phases yields a large droplet size population, while in the latter case, there are no excess phases to produce said population.^[28,31] Based on these findings, miniemulsions prepared close to the boundary of stability should belong to the Winsor type III category near the phase inversion point. On the other hand, the optical clarity of the miniemulsions located below the green line indicates the emulsifier content was elevated enough to stabilize a Winsor IV microemulsion that derived in tiny miniemulsion droplets.^[35]

It is also noteworthy that polydispersities decreased significantly between miniemulsions prepared across the boundary stability, suggesting a correlation between this variable and colloidal stability. Taking into account that higher polydispersities are generally caused by larger fractions of big droplets in the mixture, this correlation should come as no surprise since the

colloidal stability of miniemulsions is understood to be a direct consequence of their small dispersed phase sizes.^[10]

3.6. POLYMERIZATION OF LMA MINIEMULSIONS

In the previous section, the suitability to produce miniemulsions of a superhydrophobic monomer has been evaluated based on a direct and practical colloidal stability approach, whose main criterion was the minimization of the emulsifier requirements, as it is often desired in industry. A selection among the miniemulsions considered to be sufficiently stable, located along the stability boundary reported in Table II - 10, were polymerized under the conditions listed in section 3.2.3 of this chapter. A nomenclature using the monomer and emulsifier content of each miniemulsion was used to identify them; e.g. polymerization 17%-2.5% refers to the miniemulsion containing 17 wt% LMA and 2.5 wt% Brij O10.

The time-evolutions of the conversions and the dynamic light scattering results of the polymerizations are plotted in Figure II - 6 and Figure II - 7, respectively. The batch miniemulsion polymerizations were remarkably fast, reaching over 85% conversion only in the first 5 minutes for all the cases

studied. The z-average particle sizes decreased sharply as conversion progressed in that short period of time, stabilizing at values close to those of their respective final latexes in approximately 10 minutes. The DLS polydispersity values followed a similar trend, plummeting as conversion progressed and suggesting that the population of large monomer droplets obtained after the phase inversion took place disappeared in all the polymerizations. A notable exception to this trend was the reaction 23%-2.5%, whose polydispersities initially decreased but later slowly recovered; an event that could be related to the poor colloidal stability of this miniemulsion.

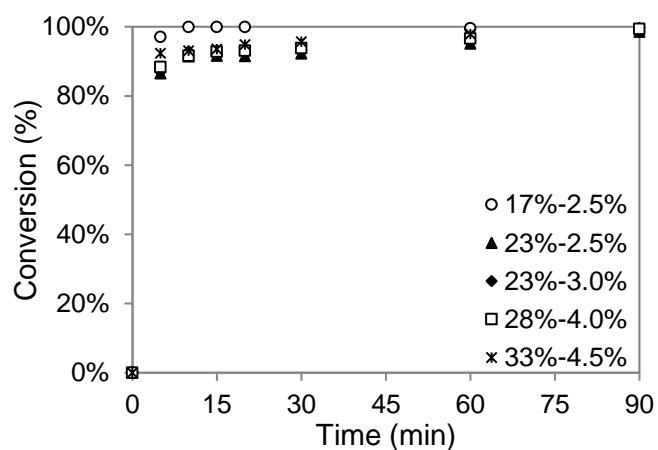


Figure III - 6. Monomer conversion time-evolution of the LMA miniemulsion polymerizations prepared by PIT

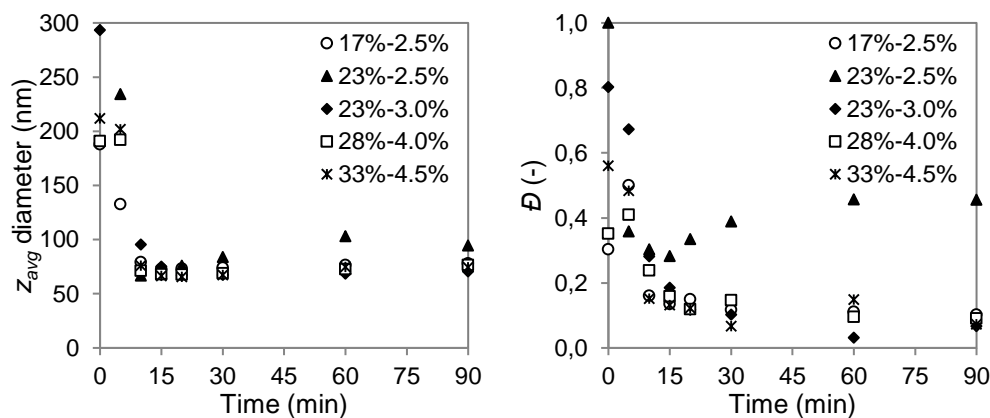


Figure III - 7. Average particle size and DLS polydispersity time-evolutions of the LMA miniemulsion polymerizations prepared by PIT

Some of the properties of the final latexes obtained from these miniemulsions are reported in **Table II - 12**. The amount of coagulum generated during the polymerizations, even if relatively low, increased together with the monomer content of the miniemulsions, despite the additional emulsifier used in the miniemulsification process. Once again, the reaction 23%-2.5% was an exception, reporting elevated coagulum contents and confirming that unstable and highly polydispersed miniemulsions lead to equally unstable latexes. None of the latexes had any gel content, and the average molecular weights measured by GPC did not reveal any differentiable characteristics among them, reporting values within typical range of emulsion polymers.

Table III - 5. Characterization of the final latexes obtained from the polymerization of the LMA miniemulsions

Reaction	Particle size*	\bar{D}	Mw	Coagulum**
23%-2.5%	95 nm	0.456	-----	33 wt%
17%-2.5%	78 nm	0.102	9.3 x10 ⁵ Da	<1.0 wt%
23%-3.0%	70 nm	0.067	8.7 x10 ⁵ Da	<1.0 wt%
28%-4.0%	76 nm	0.091	8.4 x10 ⁵ Da	2.0 wt%
33%-4.5%	74 nm	0.073	1.9 x10 ⁶ Da	8.0 wt%

*: z-average diameter obtained from dynamic light scattering

** : Based on total polymer

The differences between the initial droplet size distribution of the miniemulsions and the final particle size distributions of the latexes reported for all the experiments in Figure II - 7 could be attributed to the loss of the large droplet size population to the coagulum, although that hypothesis would not be accounting for the difference between the average size of the small droplet population and the eventual final particles.

Spornath and Magdassi^[14] also reported a similar fall of droplet to particle sizes after the polymerization for lauryl acrylate miniemulsions prepared by PIT, which they attributed to micellar nucleation triggered by trace amounts of styrene in their recipes. By eliminating those traces and increasing the

polymerization rate, the authors were only able to reach a ratio between the number of particles and droplets (N_p/N_d) of approximately 1.5, suggesting that either new nucleations or a not yet understood external factor was taking place.

It should be noted that although the miniemulsion polymerizations carried out in this section were performed at 60 °C, the dynamic light scattering measurements reported in Figure II - 7 took place at 25 °C. Taking into account that these miniemulsions were stabilized exclusively by thermo-sensitive emulsifiers, it is possible that the DLS measurements of the original miniemulsions were not representative of the events taking place in the reactor. In order to elucidate this, the 28%-4.0% LMA miniemulsion was polymerized at different temperatures between 30 and 60 °C, using the oxidant TBH and reductant SFS at a equimolar ratio in a redox initiation system. For each polymerization, the time-evolution of the conversion and the coagulum recovered at the end is presented in Figure III - 8, while the time-evolution of the average droplet/particle size is reported in Figure III - 9.

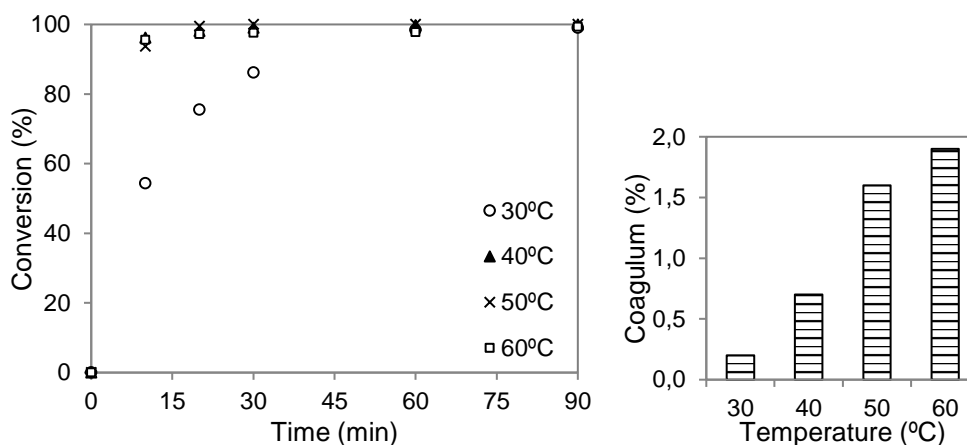


Figure III - 8. Monomer conversion time-evolution (left) and coagulum contents of the final latex (right) of the 28%-4.0% LMA miniemulsion polymerized at different temperatures

The miniemulsion polymerizations were similarly fast, with the exception of the experiment carried out at 30 °C, that despite being slower reached complete conversion by the end of the reaction. The coagulum contents were negligible at lower temperatures, barely increasing up to 2 wt% as the polymerization temperature approached 60 °C. Nevertheless, the evolution of the average size of each droplet/particle population was heavily influenced by the polymerization temperature. Miniemulsions polymerized at 50 °C and below, kept the average size of both droplet populations of the original miniemulsion relatively constant throughout the polymerization; a trend that was particularly evident for the slower polymerization at 30 °C. These results

were consistent with a predominant droplet nucleation mechanism, as would be originally expected from miniemulsions of superhydrophobic monomers.

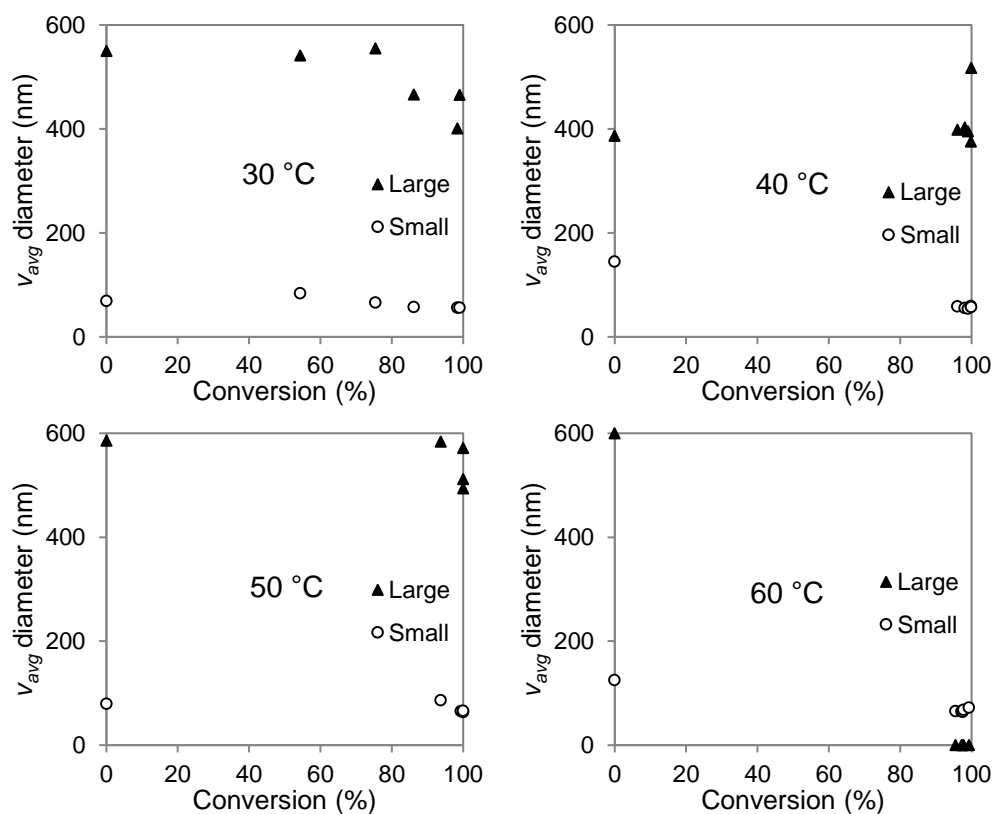


Figure III - 9. Time-evolution of the average particle size of each population of the 28%-4.0% LMA miniemulsion polymerized at different temperatures

The reduction of the droplet size of miniemulsions prepared by transitional phase inversion at conditions close to $HLD = 0$ has been reported by several authors.^[16,35-38] Nevertheless, the conditions at which the droplet size has reached a stable minimum were not those of $HLD = 0$, but rather at a given

“distance” away from this point. This has been attributed to two conflicting phenomena a system experiences as it approaches the optimal formulation point, the reduction of interfacial tension and the loss of colloidal stability; however, the variations of these two properties during this process are not alike. The changes of interfacial tension take place over a wide range of formulation conditions and have been well understood to be the consequence of the compatibilization of the emulsifier for both aqueous and oil phases. On the other hand, the loss of colloidal stability has been attributed to the trapping of surfactant within the bicontinuous microemulsion phase that appears generally at very close proximity to $HLD = 0$.^[36]

Kunieda et al.^[39] reported for a PIT system that by rapid cooling to about 25 to 30 °C away from the inversion temperature droplet coalescence was negligible and stable miniemulsions could be obtained. Following this observation and considering that the phase inversion temperatures of the miniemulsions in question were within the 82 – 87 °C range, it is possible that the polymerizations at 60 °C took place close to this optimal value, ideal for the stabilization of smaller droplets. To verify this claim, the backscattering profiles of one of the miniemulsions, 33%-4.5%, were evaluated at 30 and 60 °C for a total period of five hours and the results obtained are presented in

Figure III - 10. It was evident that the miniemulsion was less stable at 30 °C, suffering a creaming process that expanded to the lower mid-section of the vial after 5 hours; while the miniemulsion at 60 °C presented a stable homogeneous phase that expanded the length of the vial.

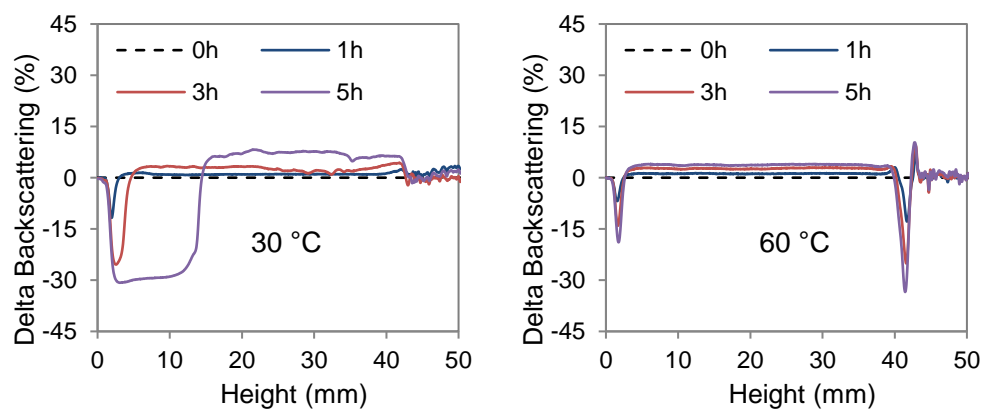


Figure III - 10. Static light backscattering profile of the 33%-4.5% miniemulsion at 30 °C (left) & 60 °C (right)

While no shear was applied during the evaluation of the backscattering profiles, after the miniemulsification stage of a typical experiment the sample is transferred to the reaction vessel at room temperature, where low shear is applied through stirring while the sample is heated up to reaction temperature. It would be at these conditions that the miniemulsion would experience diminished interfacial tensions and augmented colloidal stability, where smaller droplets could be created and polymerized.

3.7. COPOLYMERIZATION OF LMA/IBA BY PIT

As mentioned in the previous chapter, poly(lauryl methacrylate) has a very low glass transition temperature, not suitable for a protective coating despite being considered a superhydrophobic monomer, which makes copolymerization with a harder monomer necessary to create a copolymer with attractive properties. In a similar fashion, isobornyl acrylate was selected for this purpose due to its high glass transition temperature (90 °C^[40]) and hydrophobicity. A monomer ratio of 50:50 in weight and a total monomer content of 30 wt% in the final dispersion were implemented. Brij O10 was once again used as emulsifier, whose content was optimized based on the stability of the miniemulsions prepared, following the procedure described in section 3.5.

The results obtained are presented in Figure III - 11, where it was evident the miniemulsion prepared with 4 wt% of emulsifier quickly destabilized, with monomer droplets coalescing and migrating to the top of the vial just after 20 minutes at 30 °C. On the other hand, the miniemulsion prepared with 5 wt% of emulsifier was sufficiently stable to proceed to the polymerization stage. The details of the recipe as well as the results of the characterization of the miniemulsion and the final latex are reported in **Table III - 6**.

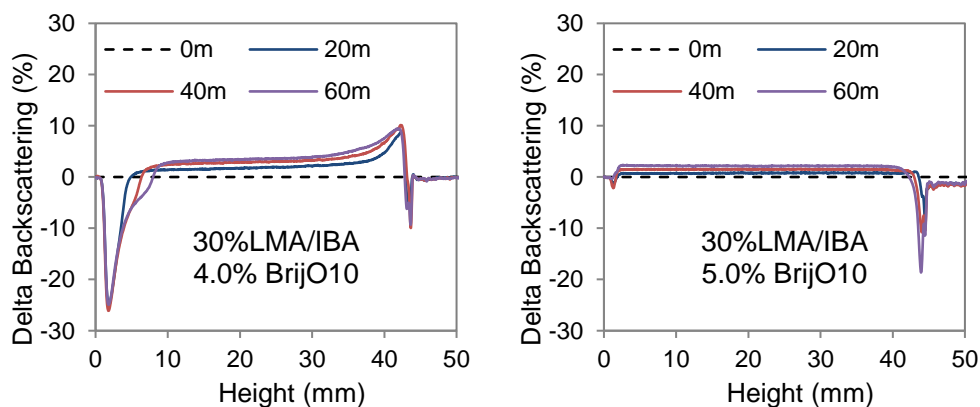


Figure III - 11. Backscattering profiles of a 30 wt% LMA/IBA miniemulsion prepared 4 wt% (left) & 5 wt% Brij O10 (right) by PIT

Table III - 6. Polymerization of the LMA/IBA miniemulsion prepared by PIT

Variable	Value	Characterization	
Temperature	60 °C	Inversion temperature	74 °C
Stirring rate	200 rpm	Droplet size	d_1 : 100 nm
Monomer content	30 wt%	(d_1, d_2, DLS)	d_2 : 425 nm
Brij O10 content	5 wt%	Particle size	78 nm
TBH content	0.5 wt%*	$(d_z, \bar{D}, \text{DLS})$	(0.033)
Redox mole ratio	0.5 ASA/TBH	Coagulum	<1 wt%
Feeding time	60 minutes	(80 μm filter)	
Batch time	30 minutes		

*: Based on monomers

The phase inversion temperature obtained for this mixture of monomers was lower than the values obtained for comparable LMA miniemulsions, which were on the 84 – 86 °C range. This is to be expected from comparatively less hydrophobic organic phases, such as the LMA/IBA monomer mixture. This

effect can also be appreciated by substituting lower EACN values, a measure of organic phase hydrophobicity, in the HLD equation (Equation I - 1). A bimodal droplet size distribution was obtained, typical of miniemulsions prepared close to the boundary of stability as discussed in section 3.5. A reduction of the average droplet to particle size, including the disappearance of the large droplet population, took place in a way similar to the LMA miniemulsion polymerizations performed at 60 °C, and it can be explained based on the same hypothesis presented in that case.

More importantly, through these results it was possible to confirm that miniemulsification by phase inversion temperature is a robust technique, capable of adapting to different mixtures of superhydrophobic monomers.

3.8. CONCLUSIONS

The feasibility of implementing miniemulsification through phase inversion as a low-energy technique to prepare polymer dispersions consisting of superhydrophobic monomers was investigated. Miniemulsions of lauryl methacrylate alone, and in mixtures with isobornyl acrylate, were carried out using alkyl polyglycoethers as emulsifiers at different conditions. The influence of the emulsifier's HLB, as well as the monomer-emulsifier-water

ratio, over the phase inversion temperature, miniemulsion stability and droplet size distribution were studied.

The phase inversion temperature of the dispersed systems was heavily influenced by the emulsifier content and HLB, decreasing as emulsifier content increased, and rising together with emulsifier HLB; making them a powerful tool for the selection of an appropriate inversion temperature in the preparation of polymerizable miniemulsions.

The monomer-emulsifier-water ratio had a profound effect on the miniemulsion colloidal stability, where higher contents of emulsifier were necessary to prepare stable miniemulsions at higher monomer contents. An iterative procedure was developed to determine the minimum emulsifier content needed to obtain stable miniemulsions at varying monomer levels. These miniemulsions presented bimodal droplet size distributions, and an inverse correlation between the broadness of the distributions and miniemulsion colloidal stability was established.

The bimodal droplet size distribution of the miniemulsions was largely preserved during the polymerizations at lower temperatures, suggesting the

predominance of a droplet nucleation mechanism, while at higher temperatures; the polymerizations resulted in monomodal latexes consisting of tiny particles. This observation was attributed to the stabilization of smaller droplets due to the decrease of interfacial tension that thermo-sensitive polyethoxylated emulsifiers experienced at temperatures 20 – 30 °C below the PIT.

3.9. REFERENCES

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