



Miniemulsion polymerization

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Abstract

Miniemulsion polymerization has recently exploded in terms of publications and the development of a wide range of useful polymer materials only accessible through this polymerization technique. In the first part of this article, the fundamental aspects involved in the preparation and polymerization of monomer miniemulsions are reviewed. The second part deals with the application of miniemulsion polymerization for the production of high solids low viscosity latexes, dispersion of polymers of well defined microstructure through controlled radical polymerization, use of catalytic polymerization in aqueous media, encapsulation of inorganic solids, incorporation of hydrophobic monomers, preparation of hybrid polymer particles, implementation of anionic and step polymerization in aqueous dispersed media, and process intensification by using continuous reactors. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Miniemulsion polymerization; Costabilizer; Ostwald ripening; Droplet nucleation; High solids low viscosity latexes; Controlled radical polymerization; Catalytic polymerization; Encapsulation; Hydrophobic latexes; Hybrid polymer particles; Continuous reactors

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1. Introduction

Polymeric dispersions are used in a wide variety of applications such as synthetic rubber, paints, adhesives, binders for non-woven fabrics, additives in paper and textiles, leather treatment, impact modifiers for plastic matrices, additives for construction materials and flocculants [1,2]. They are also used in biomedical and pharmaceutical applications such as diagnostic tests and drug delivery systems. The rapid increase of this industry is due to environmental concerns and governmental regulations to substitute solvent-based systems by water borne products, as well as to the fact that polymeric dispersions have unique properties that meet a wide range of market needs.

Commonly, these products are produced by means of conventional emulsion polymerization. In this process, monomer is dispersed in an aqueous solution of surfactant with a concentration exceeding the critical micelle concentration (CMC) and polymerization is started by means of an (most often water-soluble) initiator system. In principle, polymer particles can be formed by entry of radicals into the micelles (heterogeneous nucleation), precipitation of growing oligomers in the aqueous phase

(homogeneous nucleation), and radical entry in monomer droplets. However, monomer droplets are relatively large (1–10 μm) compared to the size of monomer-swollen micelles (10–20 nm), and hence the surface area of the micelles is orders of magnitude greater than that of the monomer droplets. Consequently, the probability for a radical to enter into the monomer droplets is very low, and most particles are formed by either homogeneous or heterogeneous nucleation.

Once they are nucleated, the polymer particles undergo substantial growth by polymerization. The monomer required for the polymerization must be transported from the monomer droplets by diffusion through the aqueous phase. In some cases, this represents a severe limitation of the conventional emulsion polymerization. Thus, water resistance of coatings prepared from dispersed polymers is significantly improved if very hydrophobic monomers, e.g. lauryl and stearyl methacrylates are incorporated into the polymer backbone. However, mass transfer of these monomers from monomer droplets to polymer particles through the aqueous phase is diffusionally controlled, and hence they cannot be readily incorporated into the polymer in conventional emulsion polymerization.

The need of mass transport of monomer through the aqueous phase would be greatly diminished if all (or at least a large fraction) of the monomer droplets were nucleated. Prevalent droplet nucleation can only occur if the surface area of the monomer droplets is large compared with that of the micelles, and this requires submicron droplet size. The word miniemulsion was coined [3] to describe submicron oil-in-water dispersions that are stable for a period ranging from hours to months. Review articles by El-Aasser et al. [4,5] summarized the work done up to 1995. The kinetics of miniemulsion polymerization has been recently reviewed by Capek and Chern [6]. This paper reviews the main aspects concerning the preparation and polymerization of monomer miniemulsions.

2. Early work

Ugelstad et al. [7] were the first to demonstrate that under conditions in which the droplet size is small enough, nucleation of monomer droplets could account for an important part of the particles formed. The method used to produce the small droplet size was inspired in previous reports showing that the presence of long chain fatty alcohols drastically increased the capacity of anionic surfactants to disperse and stabilize oil-in-water emulsions [8–11]. In those works, it was reported that the presence of fatty alcohols led to the reduction of the interfacial energy and to the formation of ordered structures far exceeding the molecular size at the oil–water interface. Ugelstad et al. [7] stirred cetyl alcohol (CA) with water and sodium lauryl sulfate (SLS) at 60 °C and then styrene was added under stirring. It was found that the miniemulsions were stable for 2 weeks. The monomer miniemulsions were polymerized at 60 °C and it was found that a large fraction of polymer particles were formed by droplet nucleation when a relatively modest amount of surfactant was used. The existence of droplet nucleation had been previously suggested by Ugelstad et al. [12] for the emulsion polymerization of vinyl chloride stabilized with a combination of anionic surfactants and fatty alcohols.

Early work also reported on the key role of both formulation and emulsification process on droplet size and stability. Ugelstad et al. [13] prepared styrene miniemulsions by stirring sodium hexadecyl sulfate/hexadecanol mixtures with water at 70 °C, then the system was cooled to 60 °C and monomer added under stirring at 600 rpm. It was found that the droplet size decreased and the stability increased as the surfactant/fatty alcohol ratio increased from 1 to 3. Miniemulsions degrade with time, the degradation being faster at higher temperatures. A mechanism for emulsification was proposed. In the first stage,

a temporary complex surfactant/fatty alcohol layer is formed which helps to emulsify the monomer. Later, the fatty alcohol diffuses towards the interior of the droplets reducing the stability of the droplets. According to this mechanism, a minimum amount of fatty alcohol is needed to saturate the droplets and have enough fatty alcohol to form the complex at the interface. This idea was supported by experiments in which the fatty alcohol was dissolved in styrene prior emulsification and only coarse unstable systems were obtained. However, the mechanism is based on the idea that the only role of the fatty alcohol is to modify the droplet surface, and as it is shown below, it has been proved that this is not the case. Polymerization of the styrene miniemulsions yielded bimodal particle size distributions (PSD), the large particles being produced through droplet nucleation. Only large fatty alcohol/surfactant ratios led to a generalized droplet nucleation. Because the fatty alcohols led to the reduction of the interfacial energy and to the formation of ordered structures, these compounds were called cosurfactants.

Azad et al. [14] found that the longer the fatty alcohol, the more stable the miniemulsion. These authors introduced two key new aspects in the process. Inspired by the works of Hallworth and Carless [15–17] and Davies and Smith [18] who had found that the stability of light petroleum, benzene and hexane emulsions was strongly improved by small amounts of hexadecane (HD), they decided to use this compound instead of a fatty alcohol to stabilize the monomer miniemulsion. It was found that with ordinary stirring equipment, addition of hexadecane did not give the rapid emulsification that could be obtained with the long chain fatty alcohols. Therefore, a more efficient homogenization system was used. It was found that when the hexadecane containing emulsions were homogenized with a Manton–Gaulin high pressure laboratory homogenizer, extremely stable monomer miniemulsions were obtained. The use of the Manton–Gaulin homogenizer did not lead to any improvement in the stability of fatty alcohol containing miniemulsions, but in this case, the stability of the miniemulsion was independent of the order in which the components of the formulation were mixed.

Davies and Smith [18] had suggested that the effect of the addition of small amounts of hexadecane might be due to the prevention of miniemulsion degradation by molecular diffusion (Ostwald ripening effect). This approach to emulsion stability was first presented by Higuchi and Misra [19], and it was based on the fact that due to the surface energy, the chemical potential of the monomer in small droplets is higher than in large droplets or plane surfaces. Consequently, monomer diffuses from small to large droplets leading to larger droplets and emulsion destabilization. Higuchi and Misra [19] predicted that the addition of a small amount of a water-insoluble compound would retard the emulsion degradation by molecular diffusion because the slow rate of diffusion of the water-insoluble compound would permit the monomer to remain essentially equilibrated among the droplets. Therefore, changes in the system would occur only as fast as the change in distribution of the slowest diffusing compound.

Durbin et al. [20] applied different degrees of emulsification (no emulsification, hand shaking, homogenization with a hand-homogenizer (Fisher Scientific), and ultrasonication) to a styrene–anionic surfactant–water system. It was found that in the absence of cetyl alcohol or hexadecane, droplet nucleation was negligible.

This early work established the basis for the miniemulsion polymerization process, namely, that energetic homogenization should be applied to reduce the size of the monomer droplets, and that these droplets should be protected against both diffusional degradation and droplet coagulation by using a water-insoluble compound and an efficient surfactant. The early work also influenced nomenclature. Thus, the water-insoluble low-molecular weight compound is often referred to as a cosurfactant in miniemulsion polymerization publications. However, with the exception of the long chain alcohols, this is a misnomer because compounds like hexadecane have no surface activity. In addition, the main

stabilizing effect of these compounds (including CA) is not a surface effect but a bulk effect. The compound responsible for stabilizing the monomer droplets against Ostwald ripening has also been called a hydrophobe to account for its water-insolubility. However, although any water-insoluble compound may retard diffusional degradation, its efficiency strongly depends on the molecular weight. Thus low-molecular weight water-insoluble compounds are much more efficient than high-molecular weight water-insoluble compounds (see Section 3.5.2.1). Therefore, the term costabilizer is used in this review to refer to low-molecular weight water-insoluble compounds, which are highly efficient in stabilizing monomer droplets against diffusional degradation. On the other hand, the use of the term hydrophobe is restricted to water-insoluble high-molecular weight compounds (e.g. polymers) that can also reduce Ostwald ripening.

3. Preparation of monomer miniemulsions

Monomer miniemulsions suitable for miniemulsion polymerization are submicron monomer-in-water dispersions stabilized against both diffusional degradation and droplet coagulation by using a water-insoluble low-molecular weight (costabilizer) compound and an efficient surfactant. The key issues in the preparation of the monomer miniemulsions are the formulation and the method of preparation. These issues as well as the often-controversial methods for the characterization of monomer miniemulsions are discussed below.

3.1. Formulations

A typical formulation includes water, a monomer mixture, a costabilizer and the surfactant and initiator systems. Table 1 shows that miniemulsions of monomers with a wide range of water solubilities have been prepared including vinyl chloride [21], vinyl acetate [22], methyl methacrylate [23–25], butyl acrylate [26], styrene [27–30], vinyl hexanoate [31], dodecyl methacrylate [32] and stearyl methacrylate [32]. In addition, multimonomer formulations have been prepared [32–39], including miniemulsions in which some amounts of completely water-soluble monomers such as acrylic acid [35,38] and methacrylic acid [36,37] have been used.

Hexadecane [26,41] and cetyl alcohol [30] are the costabilizers most often used in publications. However, these costabilizers remain in the polymer particles and may have deleterious effects on the properties of the polymer. Alduncin et al. [28] proposed to minimize these negative effects of the costabilizer by incorporating it into the polymer backbone by means of covalent bounds. A series of oil-soluble initiators with different water solubility (lauroyl peroxide, benzoyl peroxide and azobis(isobutyronitrile)) were used. It was found that only lauroyl peroxide was water-insoluble enough to stabilize styrene miniemulsion droplets. A drawback of this method is that the initiator concentration affects not only miniemulsion stability, but also polymerization rate and molecular weight distribution (MWD). In addition, it was found that rather low-molecular weights were obtained ($M_n = 20\,000\text{--}40\,000\text{ g/mol}$) [40].

N-Dodecyl mercaptan (chain transfer agent) was used as a costabilizer in the miniemulsion polymerizations of MMA [25] and S [42]. This allows one to decouple droplet stability and polymerization rate, but only low-molecular weight polymer can be produced. Water-insoluble monomers represent a more attractive alternative. Chern et al. [32,43–45] used dodecyl methacrylate and stearyl methacrylate to

Table 1
Examples of formulations for miniemulsion polymerization.

Monomer ^a	Costabilizer ^b	Surfactant ^c	Initiator ^d	Author
VC	Not disclosed	Not disclosed	H ₂ O ₂ /Cumyl hydroperoxide	Saethre et al. [21]
Vac	HD	PVOH	SPS	Wang and Schork [22]
MMA	PMMA	SLS	KPS	Reimers and Schork [24]
MMA	HD	SLS	APS	Barnette and Schork [23]
MMA	<i>n</i> -DM	SLS	KPS	Mouran et al. [25]
BA	HD	SHS	APS	Tang et al. [26]
S	CA	SLS	AMBN	Choi et al. [30]
S	HD	SLS	KPS	Hansen and Ugelstad [27]
S	LPO	SLS	LPO	Alduncin et al. [28]
S	PS	SLS	KPS	Miller et al. [29]
S	HD	pMMA- <i>b</i> -DMAEMA	AIBN	Lim and Chen [41]
S	<i>n</i> -DM	SLS	KPS	Wang et al. [42]
MMA/vinyl hexanoate	Vinyl hexanoate	SLS	APS	Reimers and Schork [31]
S/DMA, S/SMA	DMA, SMA	SLS	SPS	Chern et al. [32,43–45]
VAc/BA	HD	SHS	APS	Delgado et al. [33]
S/BA	HD, CA	SLS	APS/NaHSO ₃	Huang et al. [39]
S/MMA	HD	SLS	AIBN	Rodriguez et al. [34]
S/BA/MAA	Not disclosed	Not disclosed	Di-lauroylperoxide	Ugelstad et al. [35]
MMA/BA/MAA	Not disclosed	Not disclosed	APS	Ugelstad et al. [35]
MMA/2EHA/MAA	HD	A103/SLS	KPS	López de Arquina and Asua [36]
S/2EHA/MAA	HD	SLS/Alipal CO-436	KPS	Masa et al. [37]
VAc/MMA/BA/AA	HD	Alipal CO436/Brij 35	KPS	Unzué and Asua [38]

^a *Monomers*. AA: acrylic acid; BA: butyl acrylate; DMA: dodecyl methacrylate; 2EHA: 2-ethyl hexyl acrylate; MAA: methacrylic acid; MMA: methyl methacrylate; S: styrene; SMA: stearyl methacrylate; VAc: vinyl acetate; VC: vinyl chloride.

^b *Costabilizers/hydrophobes*. CA: cetyl alcohol; HD: hexadecane; *n*-DM: *n*-dodecyl mercaptan; PMMA: poly(methyl methacrylate); PS: poly(styrene).

^c *Surfactants*. A103: disodium salt of polyoxyethylenated nonylphenol half ester of sulphosuccinic acid; Alipal CO-436: ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol (4 ethyleneoxide)); Brij 35: C₁₂H₂₅-O-(C₂H₄O)₂₃; SHS: sodium hexadecyl sulfate; SLS: sodium lauryl sulfate; PVOH: polyvinyl alcohol; pMMA-*b*-DMAEMA: poly(methyl methacrylate-*b*-2-(dimethylamino) ethyl methacrylate block copolymer.

^d *Initiators*. AIBN: azobis(isobutyronitrile); AMBN: 2,2'-azobis-(2 methyl butyronitrile); APS: ammonium persulfate; LPO: lauroyl peroxide; KPS: potassium persulfate; SPS: sodium persulfate.

stabilize styrene miniemulsion droplets. It was found that droplet stability was higher for the more hydrophobic monomer (stearyl methacrylate), although even dodecyl methacrylate was hydrophobic enough to stabilize the miniemulsion. Reimers and Schork [31] studied the suitability of monomers of different hydrophobicity (*p*-methyl styrene, vinyl hexanoate, vinyl 2-ethylhexanoate, vinyl *n*-decanoate, and vinyl stearate) to form MMA miniemulsions. No stability measurements were reported, but the evolution of the copolymer composition during the batch polymerization of these miniemulsions suggested that stable monomer droplets were formed.

Polymers have also been used to reduce Ostwald ripening. It is worth pointing out that polymers are not true costabilizers but hydrophobes. Miller et al. [29] found that styrene miniemulsion could be

prepared by using 1 wt% of polystyrene as hydrophobe. This miniemulsion creamed rather rapidly but it was stable enough to be polymerized. Reimers and Schork [24] used poly(methyl methacrylate) to stabilize MMA miniemulsions finding that miniemulsion stability depends on polymer content and polymer molecular weight. Chern et al. [46] reported that a water-insoluble, low-molecular weight dye could offer resistance to diffusional degradation of styrene miniemulsions. Shelf life data showed that the dye is less efficient than cetyl alcohol and dodecyl methacrylate in stabilizing the miniemulsions.

Anionic [30], cationic [47], non-ionic [48] and mixed anionic/non-ionic [37,38] non-reactive surfactants, as well as reactive surfactants [49] have been used. The surfactants useful for miniemulsion polymerization should meet the same requirements as in conventional emulsion polymerization [4,50]: (i) it must have a specific structure with polar and non-polar groups; (ii) it must be more soluble in the aqueous phase so as to be readily available for adsorption on the oil droplet surface; (iii) it must adsorb strongly and not be easily displaced when two droplets collide; (iv) it must reduce the interfacial tension to 5×10^{-3} N/m or less; (v) it must impart a sufficient electrokinetic potential to the emulsion droplets; (vi) it must work in small concentrations; and (vii) it should be relatively inexpensive, non-toxic, and safe to handle. A wide variety of commercial surfactants fulfill these requirements. It is worth pointing out that the efficiency of non-ionic surfactants in conventional emulsion polymerization is reduced by the fact that they dissolve in the monomer droplets [51–53] and they are not readily available to stabilize the polymer particles nucleated by homogenous and heterogeneous nucleation. This effect is stronger at high temperatures. In this context, miniemulsion polymerization may be an alternative to enhance the efficiency of the non-ionic surfactants because at the beginning of the process, the total area of the monomer miniemulsion is much larger than that of the monomer droplets in the conventional process. Consequently, thermodynamic equilibrium will increase the fraction of surfactant at the interface droplet–water. In addition, droplet nucleation minimizes the need of surfactant mass transfer. Thermal oil soluble [28,30,34,41] and water-soluble [22,26,33] initiators, as well as redox systems [39,54] have been used.

3.2. Methods of preparation

Fig. 1 summarizes the method most often used for miniemulsion preparation. The surfactant system is dissolved in water, the costabilizer is dissolved in the monomers and mixed under stirring. Then, the mixture is subjected to high efficient homogenization. Other methods have also been reported. Thus, when a long chain alcohol (e.g. cetyl alcohol) is used as costabilizer, the long chain alcohol is first mixed with water and surfactant at temperatures higher than the melting point of the alcohol, the mixture is cooled to room temperature and sonicated to break up the gel phase. Then, monomer is added under

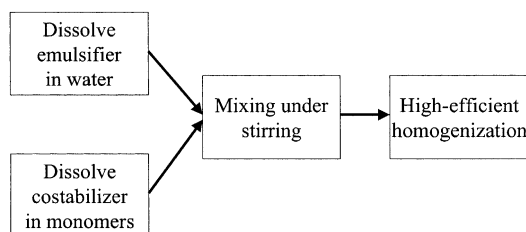


Fig. 1. Scheme for monomer miniemulsion preparation method.

stirring and the resulting mixture homogenized to form the miniemulsion [55]. The idea of forming the gel phase first comes from the early work of Ugelstad et al. [13]. These authors found that the amount of long chain alcohol needed to stabilize the miniemulsion when the fatty alcohol is first mixed with water and surfactant is smaller than that needed when the long chain alcohol is first mixed with monomer. However, this conclusion only applies to the case in which conventional stirring is used for the emulsification. Miller et al. [29] showed that the order in which the components of the formulation are mixed had no effect on the polymerization rate when an efficient homogenization device is used. This indicates that the number of miniemulsion droplets is not affected by the order of mixing.

3.3. Homogenization devices

A variety of equipment is commercially available for emulsification. The most important are rotor–stator systems, sonifiers and high-pressure homogenizers.

Rotor–stator systems and other shear devices (e.g. Ultra Turrax, Omni mixer) rely on turbulence to produce the emulsification. The minimum droplet size that can be achieved with this type of equipment depends on the size of the smallest turbulent eddy formed, which in turn depends on the geometry of the rotor–stator system and on the rotation speed.

The sonifier produces ultrasound waves that cause the molecules to oscillate about their main position as the waves propagate. During the compression cycle, the average distance between the molecules decreases, whilst during rarefaction the distance increases. The rarefaction results in a negative pressure that may cause the formation of voids or cavities (cavitation bubbles) that may grow in size. In the succeeding compression cycle of the wave, the bubbles are forced to contract and may even disappear totally [56]. The shock waves produced on the total collapse of the bubbles cause the break up of the

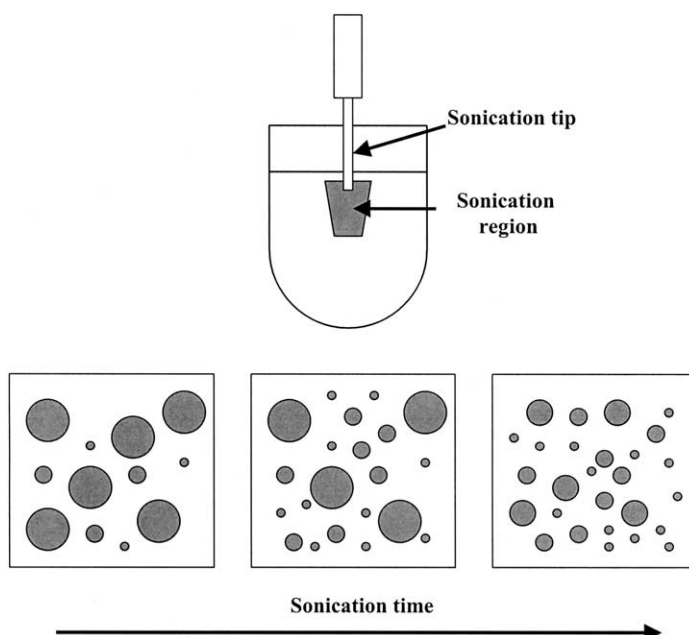


Fig. 2. Schematic of sonication process.

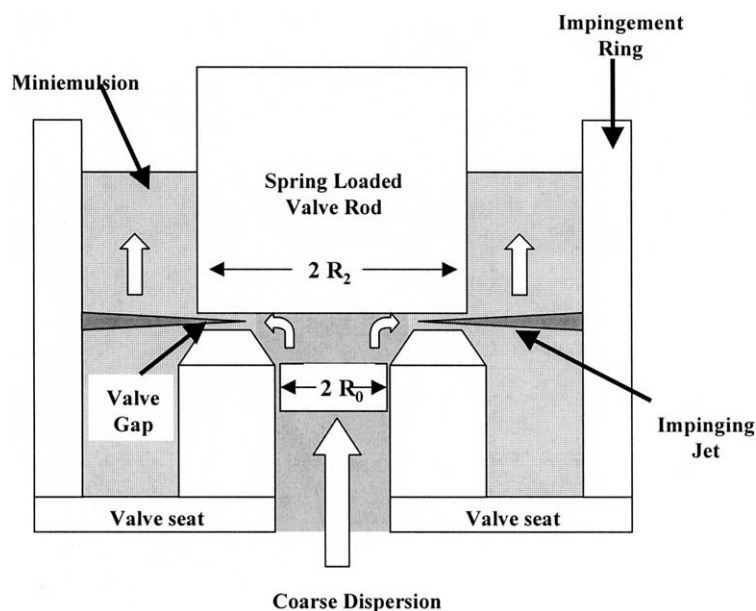


Fig. 3. Schematics of the homogenization valve of a Manton–Gaulin homogenizer.

surrounding monomer droplets. A problem associated with the sonifier is that, as shown in Fig. 2, only a small region of the fluid around the sonifier tip is directly affected by the ultrasound waves. In order to be broken up, the monomer droplets should pass through this region. Therefore, when sonication is used to form the miniemulsion, additional stirring must be used to allow all the fluid to pass through the sonication region. This process makes the miniemulsion characteristics dependent on the sonication time. Thus, there is evidence [34,57] that droplet size decreases with sonication time. The decrease is initially pronounced and later the droplet size evolves asymptotically towards a value that depends on both the formulation and the energy input.

The Microfluidizer and the Manton–Gaulin are the most commonly used high-pressure homogenizers. Both of them have in common that coarse dispersions are pressurized using a positive displacement pump, and flow through a narrow gap at high velocity. A strong pressure drop also occurs. Fig. 3 shows a schematics of the Manton–Gaulin equipment. The valve gap is controlled by the pressure applied to the valve rod. The liquid leaving the valve gap impinges on the impingement ring and it is finally discharged as a homogenized product. A second stage valve can be mounted in the equipment to maximize the intensity of the homogenization and to fine-tune the miniemulsion characteristics. In the Microfluidizer, the emulsion is forced through the interaction chamber where the stream splits into precisely defined microchannels. In the microchannels, the streams accelerate to approximately 300 m/s, are turned at right angles upon each other in a region created by an orifice plate at the same time the liquid undergoes a pressure drop. Shear, impact, and cavitation forces are focused on a small area in a very small volume of sample in any given time, which acts to break up the dispersed phase.

In high-pressure homogenizers, homogenization is mainly due to extensional forces (shear) with some contribution from cavitation and impact forces. Cavitation occurs because of the large pressure drop through the narrow gap. When the pressure drop is large enough, the vapor pressure of the liquid exceeds

Table 2

Methods used to measure the average droplet size and the droplet size distribution

Authors	Method
Azad et al. [14]	OsO ₄ staining/hardening of styrene droplets/TEM
Ugelstad et al. [35]	Free surfactant in the aqueous phase
Choi et al. [30]	Freeze-fracturing followed by replication/TEM
van Hasmsersveld [65]	Cryo-TEM
Erdem et al. [66]	Soap titration
Miller et al. [68]	CHDF
Several authors [28,32,57,69]	Light scattering
Landfester et al. [71]	SANS

the local pressure causing formation of vapor bubbles (cavities in the liquid). When bubbles implode, shock waves are generated in the liquid and these shock waves break up the dispersed droplets. Lander et al. [58] reported that in the Manton–Gaulin fluid, shear is responsible for most of the breakage, but the occurrence of cavitation was also demonstrated by detection of free radicals, which are known to be caused by cavitation [59]. Both the average droplet size and the broadness of the droplet size distribution (DSD) decrease as the number of passes through the high-pressure homogenizer increases. The decrease is relatively pronounced for the first passes and then levels off [60].

Omi et al. [61–63] used a microporous glass membrane as emulsification device. The costabilizer was dissolved in the monomer and the mixture was permeated through the membrane under pressure. The droplets come in contact with the aqueous phase immediately after the release from the pores. It is claimed that this process yields a DSD narrower than that of the other homogenization methods, but it is difficult to produce droplets smaller than 1 μm in diameter.

If small monomer droplet size is used as a measurement of the homogenization efficiency, the high-pressure homogenizers are the most efficient devices, the sonifiers and the rotor–stator systems being the least effective ones [64].

3.4. Measuring droplet size distribution

DSD is by far the most important characteristic of a monomer miniemulsion because it affects directly both miniemulsion stability and droplet nucleation. Therefore, the understanding of the mechanisms ruling miniemulsion polymerization strongly depends on an accurate determination of the DSD. Table 2 summarizes the techniques used to measure the average droplet size and the DSD. Azad et al. [14] stained/hardened styrene miniemulsion droplets with OsO₄ (styrene/OsO₄ molar ratio of 1/1.5). Samples were withdrawn after 5–10 min and placed on a formvar, carbon coated and allow to dry. The grids were examined by transmission electron microscopy (TEM). Inferior TEM pictures were obtained when the molar ratio of OsO₄/styrene was less than 1/1 or higher than 2/1 as well as when the reaction time was longer than 30 min. The spherical shape of the stained particles was assessed by shadowing the stained droplets with a 80/20 Pt/Pd alloy at an angle of 30°.

This method was unsuccessfully tried by Choi et al. [30] who pointed out that the monomer droplet sizes found by Azad et al. [14] were in the 0.4–1.5 μm range, which is much larger than that expected in the miniemulsion system, was unsuccessful. Choi et al. [30] used a freeze-fracturing technique to obtain

information on the DSD in the miniemulsion. In this technique, a small emulsion droplet was frozen by immersion in liquid nitrogen, fractured with a cold knife, shadowed and replicated with platinum/carbon. The sample was then placed in water to dissolve away the emulsion and the remaining carbon film was examined by TEM. In this method, the miniemulsion does not need to be diluted, but the path of fracture does not necessarily cross the center of the droplets, and therefore the sizes observed in the micrographs are less or equal to the actual diameters. van Hamersveld et al. [65] used cryo-TEM to study the morphology of oil–acrylate miniemulsions. A thin aqueous film was thermally fixated by vitrification in liquid ethane and imaged at $-170\text{ }^{\circ}\text{C}$. A quantitative analysis of the average droplet size was not made because of the possible occurrence of size segregation in the sample.

Ugelstad et al. [35] estimated the total surface of the monomer droplets, which is related to the droplet size and a good indication of the relative size of different systems, by measuring the amount of surfactant adsorbed on the droplets. Erdem et al. [66] extended the soap titration method [67] to the measurement of the average droplet size in miniemulsion. In this method, the miniemulsion is titrated with the surfactant to detect at what concentration the CMC is reached. The mass balance gives the amount of surfactant adsorbed. With this information plus the saturation adsorption area of the surfactant, the total surface area of the droplets (A_t) can be estimated. Then the volume-surface average droplet diameter is calculated by means of the following equation

$$d_{\text{dvs}} = \frac{6V_t}{A_t} \quad (1)$$

where V_t is the total volume of the monomer droplets. The results obtained with this method were consistent with those obtained through capillary hydrodynamic fractionation (CHDF) [68].

Miller et al. [68] used CHDF to measure the DSD of monomer miniemulsions. In this technique, the diluted miniemulsion is carried through an open capillary by a carrier fluid. A parabolic velocity profile develops in the capillary. Small droplets are able to flow closer to the capillary wall than large droplets, and hence they are carried by slower streamlines and will elute later than the large droplets. The interpretation of the fractograms is based on a calibration obtained by measuring the elution times of polystyrene latex particle standards, and it is open to discussion whether calibrations made using hard polymer particles are directly applicable to soft monomer droplets. In principle CHDF provides the DSD, but the fractograms showed by Miller et al. [68] presented small droplet size tails that might be artifacts. Nevertheless, the technique yields values of the droplet size that are in good agreement with the sizes of the polymer particles obtained after polymerization of these miniemulsions.

Light scattering has been frequently used to determine the droplets size of monomer [28,32,57,69]. This technique is very rapid and easy to implement, but by no means trouble-free. In this technique, vast dilution is needed to avoid multiple scattering. Dilution might affect the DSD, e.g. by desorption of surfactant and by dissolution of the monomer in the aqueous phase. In order to minimize this effect, the dilution is made by using the aqueous phase of the same miniemulsion (obtained by ultracentrifugation). In addition to the problems associated with sample preparation, light scattering is not well suited to determine the size distribution of polydisperse systems [70] because the inversion of the autocorrelation function is ill-conditioned. Small differences in the autocorrelation function may result in quite different size distributions after inversion namely, quite different types of size distributions correspond to almost the same autocorrelation function.

Landfester et al. [71] used small-angle neutron scattering (SANS) in an attempt to determine the droplet size of styrene miniemulsion. In addition to the fact that this is not a technique readily available,

SANS shares with light scattering the same drawback in data analysis, namely, that the raw data are fitted to a given model. Thus, Landfester et al. [71] assumed that the DSD was well represented by a Schulz–Zimm distribution, but there is no guarantee that this would be the case. For example, the DSD determined using CHDF by Miller et al. [68] cannot be well represented by a Schulz–Zimm distribution.

In conclusion, there is no direct method that guarantees the accurate determination of the DSD. This handicaps the study of the mechanisms involved in miniemulsion polymerization. The droplet size of the miniemulsion is often inferred from the PSD of the latex obtained after polymerization of the monomer miniemulsion. However, this may lead to substantial errors.

3.5. Processes controlling droplet size distribution

Monomer miniemulsions are produced by using a homogenization device and then they may be stored for some time until they are polymerized. During the homogenization stage, DSD results from the interplay between the following series-parallel processes:

- (a) Droplet break up that, depending on the homogenization device used, is caused by turbulence, cavitation, extensional forces and collision forces.
- (b) Droplet coalescence that depends on the flow pattern in the homogenization device and on the surfactant system used to stabilize the monomer droplets.
- (c) Droplet degradation by monomer diffusion (Ostwald ripening). Because of the contribution of the surface energy, the chemical potential of the monomer in small droplets is higher than in large droplets or plane surfaces. Therefore, monomer diffuses from small to large droplets. As discussed below, this process can be minimized by using costabilizers and its contribution to the DSD during the homogenization stage is likely to be modest provided that an efficient costabilizer is used. However, for less efficient costabilizers, this process may be significant as suggested by the data reported by Miller et al. [68] who found that the size of miniemulsion droplets stabilized with cetyl alcohol was not sensitive to the homogenization device used, whereas, in miniemulsions stabilized with the more water-insoluble hexadecane, droplet size decreased with the efficiency of the homogenization device.

Once they are formed, the miniemulsions may be stored for some time until they are polymerized. During this stage, droplet size may increase because of:

- (a) Droplet coalescence caused by droplet collision due to Brownian motion and van der Waals forces. The extent of this process strongly depends on the surfactant system used.
- (b) Droplet degradation by monomer diffusion, which often is the most important mechanism for the increase in size of the monomer droplets.

In what follows the basic aspects of droplet break up, droplet coalescence and Ostwald ripening are discussed.

3.5.1. Homogenization stage

3.5.1.1. Droplet break up. The mechanisms involved in droplet break up strongly depend on the type of homogenization device used: (i) high shear devices, and (ii) high-pressure homogenizers.

3.5.1.1.1. Droplet break up in high shear devices. High shear devices produce a turbulent flow in the vessel, and according to Kolmogoroff [72] the dimension of the smallest eddy is given by

$$d_{\text{eddy}} = \left(\frac{\eta_c^3}{\rho_c^3 \varepsilon} \right)^{0.25} \quad (2)$$

where η_c and ρ_c are the viscosity and the density, respectively, of the continuous aqueous phase, and ε is the rate of energy dissipation per unit mass of aqueous phase. Droplets larger than the d_{eddy} break up because opposite sides of the droplets are subjected to different velocities. The maximum size of the droplet that can survive without being broken by inertial forces is given by [73]

$$d_{\text{max}} = \rho_c^{-0.6} \sigma^{0.6} N^{-1.2} D^{-0.8} \quad (3)$$

where σ is the droplet-aqueous phase interfacial tension, N the rotor speed, and D a characteristic dimension of the shear device, e.g. the rotor diameter. Droplets smaller than the smallest eddy may break up due to viscous shear. The maximum droplet size that does not break up by viscous shear is [74]

$$d_{\text{max}} = \rho_c^{-0.5} \eta_c^{-0.5} \sigma N^{-3/2} D^{-1} f(\eta_d/\eta_c) \quad (4)$$

where η_d is the viscosity of the dispersed phase. Eqs. (3) and (4) show that the maximum droplet size decreases as the amount of surfactant in the system increases (lower σ) and more energetic shear is applied (higher values of N and D).

Baldyga et al. [75] argued that Eqs. (2)–(4) do not account for some experimental findings including (a) the decrease of the droplet size with the agitation time, and (b) the scale-up effect whereby at constant power per unit volume smaller droplets are observed in large reactors. These authors claimed that these effects could be accounted for by considering the fluctuations in the energy dissipation rate.

3.5.1.1.2. Droplet break up using sonication. Cavitation is the mechanism generally regarded as crucial in ultrasound emulsification [76]. The ultrasound waves produce cavities that may be either oscillating or transient. Transient cavities have a time-life less than the acoustic cycle and are the most common in aqueous media. Cavitation intensity is maximum when cavitation is transient. The velocity of the wall of the imploding cavity could be as high as 150 m/s and the turbulence created by this process, along with the shock waves of the collapse, may tear off the droplets near the collapsing cavity [77]. Although there is a lack of quantitative relationships relating DSD and sonication conditions, several experimental works on the effect of sonication conditions on droplet size have been reported [76–78]. In those works, it is shown that droplet size decreases with the sonication power, the sonication time and the amount of surfactant used, and increases with the volume fraction of the dispersed phase.

3.5.1.1.3. Droplet break up in high-pressure homogenizers. Droplet break up depends on the flow pattern in the homogenizer, and hence depends on the particular design of the homogenizer. In the case of the Manton–Gaulin homogenizer (Fig. 3), the coarse dispersion is fed axially into the valve seat and then accelerated radially into a small gap between the valve and the seat. Once the dispersion leaves the gap, it becomes a radial jet that stagnates on an impact ring before leaving the homogenizer. Kleining and Middelberg [79] carried out a numerical and experimental study of the homogenizer impinging jet showing that the flow is laminar. Under these conditions, monomer droplet break up will occur by extensional forces [80,81]. Moreover, a large pressure drop occurs that may cause cavitation. Cavities

from submerged jets are formed for cavitation numbers less than 0.7 [58]. The cavitation number is defined as

$$C = \frac{P - P_v}{0.5U_{\text{avg}}^2} \quad (5)$$

where P is the pressure in the impingement region, P_v is the vapor pressure of the continuous phase and U_{avg} is the velocity of the impinging jet. Lander et al. [58] calculated the cavitation number in a Manton–Gaulin homogenizer finding that under commonly used conditions, the cavitation number is less than the critical value of 0.7, namely, that cavitation occurs. These authors demonstrated the occurrence of cavitation by detecting free radicals, which are known to be caused by cavitation [59]. Lander et al. [58] reported that in the Manton–Gaulin equipment extensional forces are responsible for most of the breakage. Additional break up may occur by impact forces.

In the case of the Microfluidizer, the emulsion is forced through the interaction chamber where the stream splits into precisely defined microchannels. In the microchannels, the streams accelerate to approximately 300 m/s, are turned at right angles upon each other in a region created by an orifice plate at the same time the liquid undergoes a pressure drop. Shear, impact, and cavitation forces are focused on a small area in a very small volume of sample in any given time, which acts to break up the dispersed phase. Droplet break up is likely to occur through mechanisms similar to those occurring in the Manton–Gaulin apparatus.

The rupture of oil droplets by extensional stress has been extensively studied [82–84] in terms of the capillary number, Ca

$$Ca = \frac{\text{Hydrodynamic stress trying to break the droplet}}{\text{Interfacial stress restoring the droplet}} = \frac{\eta_c \dot{\gamma}}{\sigma/d_d} \quad (6)$$

where $\dot{\gamma}$ is the strain rate. When Ca is greater than a critical value, Ca_{crit} , the droplets break. Ca_{crit} depends on the ratio of viscosities of the dispersed and continuous phases.

$$Ca_{\text{crit}} = \frac{\eta_c \dot{\gamma} d_{\text{dmax}}}{\sigma} = f\left(\frac{\eta_d}{\eta_c}\right) \quad (7)$$

For a Manton–Gaulin homogenizer, the following equation for the maximum droplet size that is not broken up by extensional stress can be derived [58,85–87]

$$d_{\text{dmax}} = \frac{37Ca_{\text{crit}}\sigma R_2 R_0 P^{-0.35}}{2\pi\eta_c Q} \quad (8)$$

where R_2 and R_0 are geometric characteristics of the homogenizer (Fig. 3), P the pressure in the homogenizer and Q the flow rate through the homogenizer valve. Ca_{crit} for $\eta_d/\eta_c = 1$ is close to 0.6 but it strongly increases as η_d/η_c increases [87]. This means that the maximum droplet size that is not broken up by extensional stress severely increases with the viscosity of the dispersed phase.

3.5.1.2. Droplet coalescence. Shinnar and Church [88] propose a semitheoretical argument to predict the effect of coalescence in mixing vessels. Coalescence occurs when the energy of adhesion between two droplets is equal to or larger than the turbulent energy causing dispersion. In the region of inertial forces,

this yields the following equation for the minimum size of droplets that do not suffer coalescence

$$d_{\text{dmin}} = \rho_c^{-3/8} N^{-0.75} D^{-0.5} A(s)^{-3/8} \tag{9}$$

where $A(s)$ is the energy necessary to separate two adhering droplets. In the region of viscous shear the minimum droplet size is [74]

$$d_{\text{dmin}} = \rho_c^{-0.75} \eta_c^{0.25} N^{-0.75} D^{-0.5} A(s)^{-0.5} \tag{10}$$

More detailed quantitative modeling of flow induced coalescence can be achieved by considering the resistance caused by the drainage of the liquid film between the colliding droplets. In these models, the macroscopic flow brings the droplets together and hence governs the collision frequency, the contact force and the interaction time. The film drainage determines the efficiency of the collision. Janssen and Meijer [87] modeled coalescence by considering that the probability of coalescence (P_{coa}) is the product between the probability of collision (P_{coll}) and the probability of a collision being successful, which in turn depends on the drainage of the liquid film between the colliding droplets (P_{drain}):

$$P_{\text{coa}} = P_{\text{coll}} P_{\text{drain}} = \exp\left(-\frac{t_{\text{coll}}}{t_{\text{proc}}}\right) \exp\left(-\frac{t_{\text{drain}}}{t_{\text{int}}}\right) \tag{11}$$

where t_{coll} is the characteristic time for collision, t_{proc} the process time, t_{drain} the drainage time and t_{int} the interaction time. The critical parameter in Eq. (11) is the drainage time. At large separation distances, the droplets approach each other according to the velocity gradient of the external flow. At a certain distance (h_0) the droplets ‘notice’ each other and hydrodynamic interaction becomes significant. The liquid film between droplets is drained because of a contact force, F . The droplets become flattened and the drainage rate decreases as the film thickness decreases. However, at a critical film thickness (h_{crit}) the van der Waals forces take over, a sudden film rupture occurs, and the droplets coalesce. If the interaction time is sufficiently long to reach h_{crit} the droplets coalesce, otherwise the droplets separate.

The contact force depends on the flow field as well as on the forces resulting from the potential energy of interaction (given by the DLVO theory in the case of electrostatic stabilization). Therefore, it is not constant and its calculation is complicated by the fact that when droplets break up the surfactant requires some time to cover the newly formed surface, namely, the surfactant concentration at the droplet surface is not given by the adsorption equilibrium [80]. Nevertheless, valuable information can be obtained by estimating the order of magnitude of F from the external simple shear flow [87]

$$F \approx 1.5\pi\eta\dot{\gamma}d_d^2 \tag{12}$$

For a constant contact force given by Eq. (12) and partially mobile interfaces, Janssen and Meijer [87] developed the following equation for the probability of coalescence:

$$P_{\text{coa}} = \exp\left(-\frac{\pi}{8\dot{\gamma}\phi t_{\text{proc}}}\right) \exp\left(-\frac{\sqrt{3}}{8} \frac{d_d}{h_{\text{crit}}} \frac{\eta_d}{\eta_c} \text{Ca}^{3/2}\right) \tag{13}$$

In Eq. (13), the first exponential part is the probability of collision and the second the drainage probability. Eq. (13) presents a ‘coalescence window’. For too small shear rates, no collisions take place within the process time available (t_{proc}). At larger values of the shear rate, collisions do take place and the film between droplets is drained (because F also increased with $\dot{\gamma}$), leading to coalescence. At shear rates

too large, numerous collisions take place, but these are too fast to get the film drained so that coalescence will not occur. This coalescence window depends on the droplet size. Large droplets do not coalesce easily because they need more time to drain the liquid film.

For sufficiently long process times, Janssen and Meijer [87] assumed that coalescence occurs when $t_{\text{int}} = t_{\text{drain}}$. This allows calculation of the critical droplet size, below which coalescence takes place, and above which it does not. The critical droplet size depends on the type of interface (immobile, partially mobile, and fully mobile). For a partially mobile interface, the critical droplet diameter is:

$$d_{\text{dmin}} = 2 \left(\frac{4}{\sqrt{3}} h_{\text{crit}} \right)^{2/5} \left(\frac{\eta_{\text{d}}}{\eta_{\text{c}}} \right)^{-2/5} \left(\frac{\eta_{\text{c}} \dot{\gamma}}{\sigma} \right)^{-3/5} \quad (14)$$

3.5.1.3. Interplay between droplet break up and coalescence. During the formation of the miniemulsion both break up and coalescence occur, and the DSD results from the interplay between these processes. If a high-pressure homogenizer is considered, Eqs. (8) and (14) provide estimations of the maximum droplet size that does not break up and the minimum droplet size that does not coalesce, respectively. Fig. 4 depicts these limits for the case in which $h_{\text{crit}} = 3$ nm, and equal viscosities of the continuous and dispersed phase. It can be seen that for $\eta_{\text{c}} \dot{\gamma} \sigma < 10^8$, a range of droplet size exists in which droplets do not break up nor coalesce. Assuming a parabolic velocity profile and the values of the average velocity in the impinging jet given by Lander et al. [58], the value of $\eta_{\text{c}} \dot{\gamma} \sigma$ with $\eta_{\text{c}} = 10^{-3}$ Pa s and $\sigma = 2 \times 10^{-3}$ N/m is in the order of 10^{-7} . According to Fig. 4 this should give droplets with sizes between 50 and 100 nm and narrow DSD because droplets smaller than 50 nm will coalesce and bigger than 100 nm will break up. Although these values are only illustrative because of the limitations of the models used and the uncertainties in the parameter values, they show that rather small droplets with narrow DSD can be obtained in the impinging jet. However, once the fluid leaves the impinging jet, the fluid enters in a zone of low shear (low value of $\eta_{\text{c}} \dot{\gamma} \sigma$) where only coalescence occurs, yielding to an increase of both droplets size and polydispersity index (PI). Janssen and Meijer [87] have presented a 2-zone model to account for this phenomenon.

For high shear devices, the interplay between break up and coalescence presents a plot similar to Fig. 4. In those devices, shear is related to the rotor speed. For low turbulence (low N) a region exists in

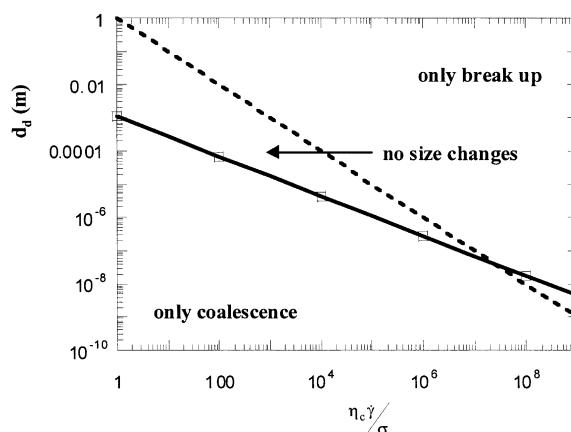


Fig. 4. Interplay between droplet break up and coalescence.

which droplets do not break up nor suffer coalescence. This is the region used for suspension polymerization (employing regular stirrers), but the droplet size is too big for miniemulsions. Miniemulsions require high turbulence, and hence they are formed in the region in which a dynamic equilibrium between break up and coalescence is established. Models based on population balances to predict the droplets size distribution have been reported [89,90]. Unfortunately, they are complex and involve parameters that are not always available.

3.5.1.4. Droplet degradation by diffusion during homogenization. Due to the surface energy, the monomer chemical potential in small droplets is higher than in large droplets or plane surfaces. Consequently, monomer diffuses from small to large droplets leading to larger droplets and emulsion destabilization. Higuchi and Misra [19] predicted that the addition of a small amount of a costabilizer retards the emulsion degradation by molecular diffusion because the slow rate of diffusion of the costabilizer permits the monomer to remain essentially equilibrated among the droplets. This means that the fast diffusing compound (monomer) reaches pseudo-equilibrium conditions, implying that monomer diffusion is not diffusionally controlled. The issue of monomer diffusion rate in miniemulsion polymerization was considered by Delgado et al. [91,92] who modeled miniemulsion copolymerization considering the possibility of rate determining monomer transfer from droplets to polymer particles. Although these authors obtained good agreement between the experimental results and the model predictions, no definitive conclusion was reached regarding the importance of the resistance associated with monomer mass transfer from droplets to polymer particles. Rodriguez et al. [93] attempted to determine the mass transfer coefficients between two miniemulsions separated by a membrane. However, the high resistance of the membrane did not allow the determination of the mass transfer coefficients. Rodriguez [69] measured the mass transfer coefficients of styrene and methyl methacrylate at the interface between miniemulsion droplets and aqueous phase, reporting values for these coefficients based in the oil phase between 1.6×10^{-9} and 3×10^{-9} m/s. If the mass coefficients were referred to the aqueous phase, those values would be in the order of 10^{-6} and 10^{-7} m/s for styrene and methyl methacrylate, respectively. Rodriguez et al. [94] showed by simulation that these coefficients were much higher than those required to hold the system under thermodynamic equilibrium. Therefore, the degradation of monomer droplets by diffusion is the result of the interplay between the kinetics of the diffusion of the costabilizer and the thermodynamics ruling the concentration of monomer in the droplets.

The costabilizer should be chosen in such a way that the characteristic time for its diffusion is much longer than the characteristic time for the use of the miniemulsion. The residence time of the dispersion in the homogenization device is short compared to the storage and polymerization times, and hence it may be safely assumed that droplet degradation by diffusion plays no significant role when an efficient costabilizer is used.

3.5.2. Storage stage

During the time elapsed between miniemulsion preparation and polymerization, the DSD may vary because of coalescence caused by droplet collision due to Brownian motion and van der Waals forces and because of droplet degradation by monomer diffusion. The extent of the coalescence may be greatly reduced by using a good surfactant system and this process will not be considered here. On the other hand, the extent of the droplet degradation by monomer diffusion can be minimized by including a costabilizer in the formulation [19], and all miniemulsion formulations include such a compound. The

main effect of the costabilizer is to modify the thermodynamics ruling the partitioning of the monomer, which in turn influences the monomer mass transfer rate.

3.5.2.1. Thermodynamic basis for the stabilization of monomer miniemulsions against degradation by diffusion. The partial molar Gibbs free energy of monomer in a monomer droplet containing a water-insoluble compound is given by the following equation [35,95–97]

$$\frac{\overline{\Delta G_m}}{RT} = \ln(\phi_m) + (1 - m_{mh})\phi_h + \chi_{mh}(\phi_h)^2 + \frac{2\bar{V}_m\sigma}{rRT} \quad (15)$$

where ϕ_m and ϕ_h are the volume fractions of monomer and costabilizer in the monomer droplets, respectively, m_{mh} the ratio of the molar volume of monomer (\bar{V}_m) to that of costabilizer (\bar{V}_h), χ the interaction parameter, σ the droplet–water interfacial tension, and r the volume of the droplet.

In order to gain an understanding of the effect of the costabilizer, let us consider first a monomer droplet containing some costabilizer in the presence of a pool of pure monomer forming a plane surface. Under these conditions, $\overline{\Delta G_m} = 0$ and the droplets reach maximum equilibrium swelling. Fig. 5 shows the maximum swelling as a function of the type of costabilizer and the radius of the monomer droplet. In this plot, $m_{hm} = 0$ represents a polymer (hydrophobe), whereas $m_{hm} = 0.5$ represents a costabilizer with a molecular weight about twice of that of the monomer. It can be seen that low-molecular weight water-insoluble compounds (costabilizers) lead to super-swelling. On the other hand, a much more modest swelling can be achieved when polymer (hydrophobe) is used. Fig. 5 shows that swelling increases with droplet size. It should be emphasized that in the absence of costabilizer, the droplets will disappear by diffusion of the monomer from the droplet to the pool of monomer.

Fig. 5 has also important consequences for some of the formulations used to prepare miniemulsions. Thus, a problem associated with low-molecular weight costabilizers is that these compounds can have deleterious effects on application because they can leach out after film formation. Therefore, high-molecular weight costabilizers can be beneficial and polymers are used. However, Fig. 5 shows that a miniemulsion containing a few percent of polymer (typically 2–4%) is not stable because its maximum swelling for the parameters used in Fig. 5, is about 80% of monomer and 20% of polymer. This means

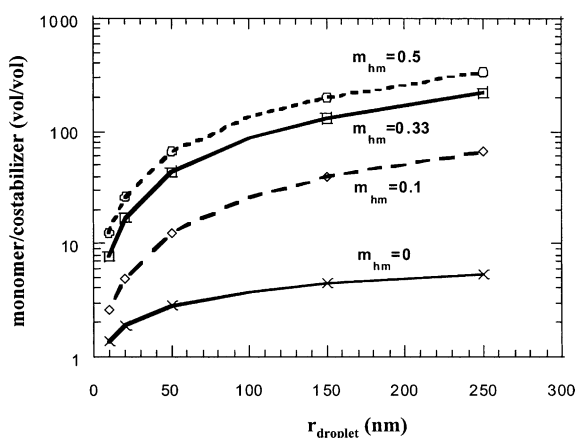


Fig. 5. Effect of droplet size and type of costabilizer on maximum swelling. $\chi = 0.5$; $\bar{V}_m = 10^{-4} \text{ m}^3/\text{mol}$; $\sigma = 5 \times 10^{-3} \text{ N/m}$; $T = 333 \text{ K}$.

that a 500 nm in diameter monomer droplet initially containing 2% of polymer will lose 92% of the monomer reducing its size to 230 nm. The monomer will form a separate pure monomer phase.

In the homogenization stage, droplets of different sizes are formed, but for the sake of simplicity let us assume that two types of droplets, with initial radius r_{10} (small droplets) and r_{20} (large droplets) and with the same concentration in terms of monomer and costabilizer may represent the distribution. During storage, because of its higher chemical potential in the small droplets, monomer diffuses from small to large droplets until the pseudo-equilibrium is reached (the term pseudo-equilibrium is used to emphasize that it will be modified if the costabilizer diffuses). The pseudo-equilibrium is reached when

$$\ln(\phi_{m1}/\phi_{m2}) + (1 - m_{hm})(\phi_{h1} - \phi_{h2}) + \chi_{mh}((\phi_{h1})^2 - (\phi_{h2})^2) + \frac{2\bar{V}_m\sigma}{RT} \left(\frac{1}{r_{1e}} - \frac{1}{r_{2e}} \right) = 0 \quad (16)$$

where r_{1e} and r_{2e} are the radius of small and large droplets, respectively, at pseudo-equilibrium. These values are different from r_{10} and r_{20} ($r_{10} > r_{1e}$ and $r_{20} < r_{2e}$). Fig. 6 shows the effect of the type of costabilizer and the r_{20}/r_{10} ratio on the size reduction of the small droplets. It can be seen that the higher the molecular weight of the costabilizer and greater the size ratio, smaller is the pseudo-equilibrium size of the small droplets. In particular, when a costabilizer of molecular weight about three times that of the monomer is used, a droplet with an initial diameter of 30 nm will become a droplet of about 16 nm in diameter when it is in the presence of droplets of $r = 200$ nm. This means that more than 80% of the monomer contained in the small droplets diffuses to the large droplets. The deswelling is even more pronounced when a polymer is used. Fig. 6 also shows that the effect of the size of the large droplets is very pronounced for radius slightly larger than the size of the smaller droplet, but later the effect levels off.

Fig. 7 shows that the extent of deswelling depends on the size of the small droplets. The larger the size the less monomer is lost by these droplets. Droplets larger than 50 nm in diameter only lose a small fraction of monomer when they are stabilized with a good costabilizer. In this case, the broadness of the DSD is important because the deswelling increases as the size ratio increases up to a value of about 4–5. Higher values do not significantly increase deswelling. When polymer is used as hydrophobe, the

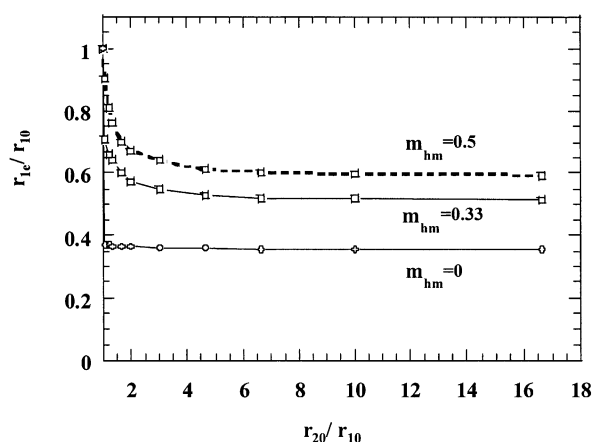


Fig. 6. Effect of the type of costabilizer and droplet size ratio on the deswelling of small monomer droplets. $r_{10} = 15$ nm; $\phi_h = 0.02$; $\chi = 0.4$; $\bar{V}_m = 10^{-4}$ m³/mol; $\sigma = 5 \times 10^{-3}$ N/m.

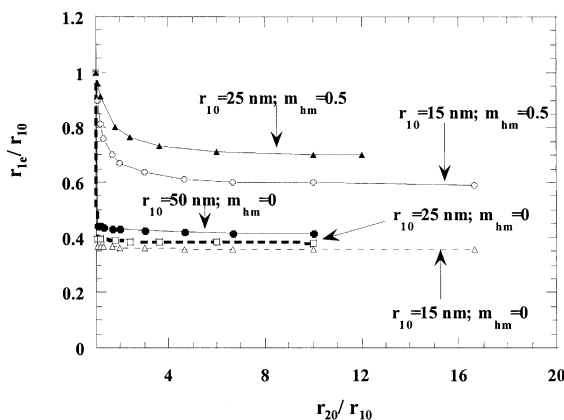


Fig. 7. Effect of the radius of the small droplet on the deswelling of small monomer droplets. $m_{hm} = 0.5$; $\phi_h = 0.02$; $\chi = 0.4$; $\bar{V}_m = 10^{-4} \text{ m}^3/\text{mol}$; $\sigma = 5 \times 10^{-3} \text{ N/m}$.

deswelling is very pronounced even for monomer droplets of 100 nm in diameter. Thus, in the presence of another droplet with an initial size of 120 nm, a monomer droplet with an initial diameter of 100 nm will become a droplet of about 40 nm in diameter. In this case, the broadness of the DSD is not very important because most of the deswelling occurs for very small differences in droplet size that cannot be avoided in any miniemulsification process.

Fig. 8 presents the effect of the amount of costabilizer on the diffusional degradation of monomer droplets. It can be seen that droplet stability substantially increased when a small amount of costabilizer is incorporated in the droplets. Initial volume fractions of costabilizer higher than 0.04 only lead to a slight increase of the droplet stability.

The previous paragraphs refer to thermodynamic equilibrium and describe the situation that the

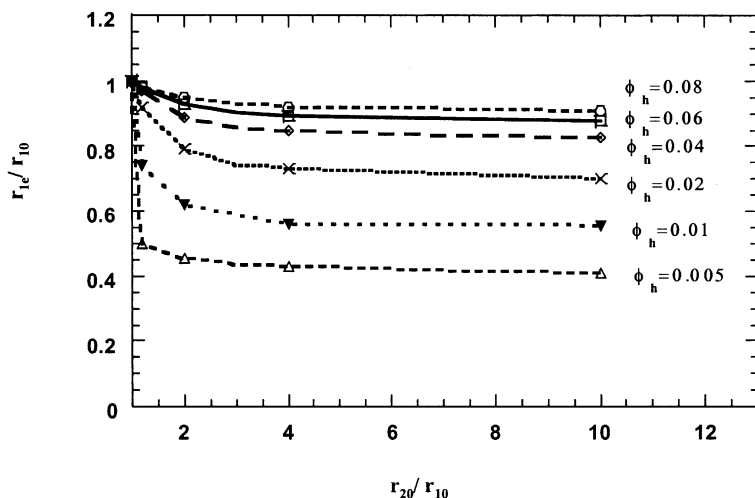


Fig. 8. Effect of the volume fraction of costabilizer on the stability of the monomer droplets. $r_{10} = 25 \text{ nm}$; $m_{hm} = 0.5$; $\chi = 0.4$; $V_M = 10^{-4} \text{ m}^3/\text{mol}$; $\sigma = 5 \times 10^{-3} \text{ N/m}$.

system will reach after diffusion of the monomer from small to large droplets. In this context, it is worth pointing out that monomer diffusion is a kinetic process that takes some time. As the driving force for monomer diffusion is the difference between chemical potential of the monomer in the small droplets and that in the large droplets, thermodynamics affect not only the final state but also the rate at which Ostwald ripening occurs. The reduced monomer diffusion rate may be the reason why miniemulsions stabilized with small amounts of polymers do not degrade rapidly [98] and can be polymerized successfully [29]. Another possible reason is that the formation of a separate monomer phase requires the nucleation of very small droplets, in which the chemical potential of the monomer is very high, and this may act as an activation energy barrier for the formation of a separate pure monomer phase.

It can be concluded that the main factor affecting Ostwald ripening is the nature of the costabilizer. The ideal structure being a low-molecular weight compound completely insoluble in water. Volume fractions of 2–4% are enough to avoid deswelling and no substantial benefit is gained from increasing this amount. When a good costabilizer is used, the DSD produced during homogenization is very important. Miniemulsions with narrow DSDs of average diameters greater than 50 nm are only mildly affected by Ostwald ripening, whereas a stronger effect is expected for both broad DSDs and small droplet sizes. When a hydrophobe (e.g. polymer) is used, strong Ostwald ripening is expected for all DSDs, the effect of the distribution being negligible.

3.6. Effect of the preparation variables on the droplet size distribution and droplet stability

In the paragraphs above, it was shown that the complex processes occurring during homogenization and storage of the miniemulsion determine the DSD. In what follows, the effect of the preparation variables on the DSD will be summarized by considering both the theoretical predictions and the experimental findings. Homogenization and aging will be considered separately.

3.6.1. Homogenization

As it is discussed above, different mechanisms of monomer droplet break up are operative in the different homogenization devices. Therefore, it is not unexpected that droplet size is strongly affected by the choice of the homogenizer. At equal power applied per unit volume, the high-pressure homogenizers are the most efficient devices giving the smallest droplets, the sonifiers, and the rotor–stator systems being the least effective ones [64]. Results reported by different researchers support this conclusion, although it should be pointed out that the data might have been obtained using different power/volume ratios in each device. Thus, Tang et al. [99] prepared styrene miniemulsions with hexadecane as costabilizer and SLS as surfactant using three emulsification devices: (1) Omni mixer (shear), (2) sonifier, and (3) Microfluidizer. These miniemulsions were polymerized in batch. It was found that the final particle sizes ranged as: $d_{p\text{Microfluidizer}} < d_{p\text{sonifier}} < d_{p\text{Omni mixer}}$. In addition, the polymerization rate using the miniemulsion prepared with the Microfluidizer was much faster than that of the Sonifier, which in turn was faster than that using the Omni mixer. Huang et al. [39] found that sonication was more effective than high shear. Miller et al. [68] found that the droplet size of toluene miniemulsions prepared using hexadecane and the Microfluidizer were smaller than those prepared using hexadecane and the sonifier. On the other hand, the size of miniemulsion droplets prepared using cetyl alcohol did not appear to be sensitive to which homogenizing device was

used [68]. This suggests that cetyl alcohol is not sufficiently water-insoluble to stabilize the small droplets initially formed in the Microfluidizer.

Eqs. (8) and (14) and Fig. 4 predict that, for a given homogenization device, droplet size decreases with the power applied per unit volume. This agrees with the results reported by Saethre et al. [21] who found that droplet size decreased with homogenization pressure using a Manton–Gaulin homogenizer. Similar results have been obtained by do Amaral and Asua [60]. Chern et al. [43] found that at low sodium lauryl sulfate concentrations the homogenization pressure of the Microfluidizer had no effect on the droplets size of miniemulsions stabilized with SLS using stearyl methacrylate as costabilizer. At higher SLS concentrations, the droplet size decreased with homogenization pressure. Fontenot and Schork [57] found that the droplet size also decreases with power/volume ratio applied by sonication. Fig. 4 also predicts that an increasing power/volume ratio leads to narrower DSDs. This prediction was experimentally checked by do Amaral and Asua [60] who found that increasing the operating pressure of a Manton–Gaulin homogenizer led to a narrower DSD as estimated from dynamic light scattering measurements.

In the case of ultrasound homogenization, there are many reports showing that droplet size decreases with sonication time [34,39,57,100,101]. The decrease is initially pronounced and is exponential for long sonication times. The initial decrease is to a large extent associated with the geometry of the sonicator. As shown in Fig. 2, only a small region of the fluid around the sonifier tip is directly affected by the ultrasound waves. In order to be broken up, the monomer droplets should pass through this region. Therefore, when sonication is used to form the miniemulsion, additional stirring must be used to allow all the fluid to pass through the sonication region and some time is required to pass all the vessel volume through the sonication region. Probably, the size reduction is not completed in a single pass through the sonication region and several passes are required. A similar phenomenon was observed in the case of high-pressure homogenizers because both the droplet size and the broadness of the DSD decrease with the number of passes through the homogenizer [60].

According to the calculations in Fig. 8, it is expected that droplet stability will improve significantly when small amounts of costabilizer are added (up to 2–4% based on monomer), additional amounts providing only marginal benefits. In addition, small droplets require higher concentrations of costabilizer to achieve the same stabilization (Fig. 7). These predictions agree with the results reported by Delgado et al. [33] who found that at low hexadecane concentrations (up to about 1.5% for large droplets and 5.7% for small droplets), the droplet size of vinyl acetate–butyl acrylate miniemulsions decreased substantially, but at higher hexadecane concentration droplet size was independent of the amount of costabilizer. Fontenot and Schork [57] reported that droplet size decreased with hexadecane concentration up to about 3 wt% and then leveled off. Similar effects have been reported with other costabilizers. Thus, Mouran et al. [25] and Wang et al. [42] found that droplet size decreased with the concentration of dodecyl mercaptan used as costabilizer. Miller et al. [68] reported that droplet size decreased with cetyl alcohol content. Chern and Chen [32] reported that droplet size decreased with the concentration of the alkyl methacrylate used as both comonomer and costabilizer. A result that does not follow the pattern is that reported by Landfester et al. [101] who did not find any effect of the hexadecane concentration in the range 0.33–6.2 wt%.

The droplet size also decreased with the concentration of polymeric hydrophobes. Reimers and Schork [102] reported that increasing concentrations of poly(methyl methacrylate) led to smaller droplet size. For miniemulsions stabilized with PMMA, Wang et al. [103] found that droplet size decreased with the amount of alkyd resin used in the formulation. This result suggests that the alkyd resin reinforced the

action of the PMMA, although in the absence of PMMA the alkyd resin was not able to stabilize small droplets, perhaps due to a poor compatibility with the monomer.

Fig. 5 shows that the smaller the molecular weight of the costabilizer the higher the swelling, and hence the better the stabilization of the monomer droplets against Ostwald ripening. Miller et al. [29] based on the relative creaming rates of the miniemulsions prepared with different amounts of cetyl alcohol and polymer, concluded that in agreement with the theoretical predictions, the droplet sizes range as:

$$d_{d(\text{CA})} < d_{d(\text{CA}+0.05\% \text{ polymer})} < d_{d(\text{CA}+0.5\% \text{ polymer})} < d_{d(\text{CA}+1\% \text{ polymer})} \quad (17)$$

In the thermodynamic calculations, it was assumed that the costabilizer was completely insoluble in water. However, most of the costabilizers used have a finite water-solubility. Under these circumstances, the costabilizer, which also has a higher chemical potential in the small particles, may diffuse to the large particles. Consequently, miniemulsions degrade to some extent. There are conclusive data showing that the higher the water solubility of the costabilizer the larger the droplet size. Thus, Chern and Chen [32] prepared miniemulsions using four different costabilizers: hexadecane (water solubility = 1.14×10^{-9} l/l) [104], stearyl methacrylate (water solubility = 3.23×10^{-9} l/l) [43], dodecyl methacrylate (water solubility = 1.38×10^{-8} l/l) [43] and cetyl alcohol (water solubility = 5.77×10^{-8} l/l) [43], finding that the droplet size ranged as:

$$d_{d(\text{HD})} < d_{d(\text{SMA})} < d_{d(\text{DMA})} < d_{d(\text{CA})} \quad (18)$$

Ugelstad et al. [35] and Miller et al. [68] also found the droplet size of miniemulsions stabilized with hexadecane is smaller than that of the miniemulsions containing cetyl alcohol. Alduncin et al. [28] used a series of initiators of different water solubility finding that only lauroyl peroxide gave a small enough droplet size. Benzoyl peroxide and AIBN are too water-soluble and led to large monomer droplets.

In the early literature, strong emphasis was given to the order in which the components of the formulation were mixed when cetyl alcohol was used as costabilizer [13]. In these works, homogenization was carried out using simple agitation, and hence the formation of small aggregates of long chain alcohol and surfactant that were later swelled with monomer was critical. Similar results have been obtained more recently [54]. However, Miller et al. [68] have demonstrated that the order of addition of the components of the formulation has no effect on DSD when an efficient homogenizer is used.

Eq. (8) predicts that the maximum droplet size that is not broken up by extensional stress strongly increases with the viscosity of the dispersed phase (Ca_{crit} strongly increases with η_d [87]). This prediction agrees quite well with the experimental findings reported by Blythe et al. [105]. These authors prepared miniemulsions costabilized with hexadecane and 1 wt% of polymer. Two polystyrenes of different molecular weight were used ($M_n = 39\,000$ g/mol, $M_n = 206\,000$ g/mol). The viscosity of the oil phase of the miniemulsion prepared with the high-molecular weight polymer was 330% higher than that of the low M_n and yielded larger droplet sizes. Similar results showing the effect of oil phase viscosity on droplet size have been reported by Saethre et al. [21] using a Manton–Gaulin homogenizer. Anderson et al. [106] prepared styrene miniemulsions using polystyrene of different molecular weights as hydrophobes. The polystyrene molecular weights ranged from 1000 to 1 000 000 g/mol. It was found that the droplet size increased from 300 nm for the smallest molecular weight to about 560 nm for the highest molecular weight. Although these results qualitatively agree with the effect of the droplet viscosity predicted by Eq. (8), the authors stated that the increasing viscosity could not account for such a large increase in droplet size, and that there was a contribution of the effect of molecular weight

on swelling thermodynamics. A 1 000 000 g/mol polymer would be a hydrophobe, whereas a 1000 g/mol polymer would have some costabilizer character and hence it would stabilize smaller droplets.

The surfactant concentration influences droplet coalescence through both the contact force (lowering it because of the electrostatic and steric interactions) and reduction of the critical film thickness. This leads to a smaller critical droplet size below which coalescence takes place and above which it does not, and hence smaller droplets can be stabilized. There is a large body of data showing that droplet size decreases by increasing surfactant concentration [32,39,41,42,57,68,102]. The decrease of the droplet size is very pronounced at low surfactant concentrations and reaches a minimum size that cannot be significantly reduced by increasing further the surfactant concentration. Eqs. (8) and (14) show that surfactant concentration has a strong effect on droplet coalescence but a very weak one on droplet break up. The initial droplet size decrease with increase in the surfactant concentration is due to a reduction of the coalescence. However, the size cannot be reduced below the critical size for break up, and for a given homogenization device, the size depends mostly on the power/volume ratio. Therefore, the only way to reduce further the droplet size is to increase the energy applied or to apply it more efficiently by using a different homogenization equipment. This brings two issues of practical importance: (i) can micelles exist in miniemulsions? and (ii) can the size of the monomer droplets be reduced indefinitely? These issues are of practical importance because the applications of the miniemulsions are strongly linked to droplet nucleation. Droplet nucleation will be jeopardized if micelles are present in the system (as micellar nucleation will be operative) and if droplet size is too large (because the droplets will not compete efficiently for the radicals in the aqueous phase and homogeneous nucleation will occur). Micelles will exist in a miniemulsion if the surface area that can be covered by the surfactant exceeds the surface area of the droplets that can be produced by the homogenization device. On the other hand, Fig. 4 shows that droplet size cannot be reduced indefinitely because the lines of droplet break up and coalescence cross each other, and although the droplets are breaking up they coalesce. It is worth pointing out that as the miniemulsion leaves the homogenization device, the shear rate decreases and the minimum critical size for coalescence increases. In some cases, post-stabilization of the miniemulsion with additional surfactant just after homogenization minimizes coalescence [101].

There is some debate about the existence of an optimal surfactant/costabilizer ratio. Chou et al. [3,107] showed that the stability of miniemulsions prepared by simple stirring and stabilized with hexadecyltrimethylammonium bromide and cetyl alcohol was best for surfactant/costabilizer molar ratios between 1/1 and 1/3. Grimm et al. [108] described that the most stable miniemulsions (using sodium lauryl sulfate and cetyl alcohol, and formed by simple stirring) were formed at surfactant/costabilizer molar ratios between 1/1 and 1/3. In addition, better stability was observed when the alcohol had the same chain length as that of the surfactant. Choi et al. [30] reported that the SLS/cetyl alcohol molar ratio giving the most stable miniemulsions prepared using the Microfluidizer was 1:3. The existence of this optimal ratio is likely linked to the surface activity of cetyl alcohol because no optimal costabilizer/surfactant ratio has been found in miniemulsions stabilized by hexadecane and sodium hexadecyl sulfate [33].

In styrene miniemulsions stabilized with sodium lauryl sulfate and hexadecane, Landfester et al. [101] found that using a constant monomer/surfactant/costabilizer ratio the droplet diameter increased with the solids content. This result is accounted for by Eq. (13) that shows that the probability of collision (and consequently that of coalescence) increases with the volume fraction of the dispersed phase. Therefore, it is expected that the droplet size increases with solid content. Fontenot and Schork [57] provided additional indirect experimental evidence of the effect of the solids

content on the droplet size: in miniemulsions prepared by sonication the creaming rate increased with the solids content.

There are some conflicting reports on the effect of the water-solubility of the monomer on the droplet size. Thus, Rodriguez et al. [93] found that the droplet size of styrene miniemulsions costabilized with hexadecane was larger than that of MMA miniemulsions. On the other hand, using the same costabilizer, Fontenot and Schork [57] found that for the rest of conditions constant, styrene miniemulsions had smaller droplet size than methyl methacrylate miniemulsions, which in turn were smaller than vinyl acetate miniemulsions. This effect was attributed to different rates of droplet degradation by monomer diffusion. However, this implies that monomer diffusion is the rate-determining step, and there are data showing that this is not the case for miniemulsions [69,91–93]. Another possibility is that the different monomers have different interaction parameter with hexadecane and this will certainly modify the swellability of the droplets.

Huang et al. [39] found that the creaming rate of the miniemulsion varied with the emulsification temperature. A maximum of stability (minimum droplet size) was found for the miniemulsion prepared at 40 °C.

3.6.2. Aging

The stability of miniemulsions, once they are prepared, is important because the success of the miniemulsion polymerization process relies on nucleating the monomer droplets, and hence they should be preserved. In this regard, one should be concerned about the stability of the miniemulsion during the time elapsed between the preparation and the polymerization, as well as during the polymerization process. Because of the difficulty of implementing experimental techniques to monitor the monomer droplets during polymerization, most of the studies on miniemulsion stability have been carried out under non-polymerizing conditions. Nevertheless, useful information can be obtained from those experiments.

Once they are formed and under non-polymerizing conditions, monomer miniemulsions may degrade because of monomer diffusion, costabilizer diffusion, settling or creaming, and droplet coalescence. It has been found that monomer diffusion is fast as compared with the other processes [69,91–93], and therefore monomer concentration in the droplets is under pseudo-equilibrium conditions.

Settling and creaming depend on the droplet size and DSD. The smaller the droplets, the more stable is the miniemulsion towards settling and creaming. Therefore, all the variables discussed in the previous paragraphs that result in smaller droplets (costabilizer concentration, surfactant concentration, efficient homogenization devices, high power/volume ratio, sonication time, number of passes through the high pressure homogenizer, low-molecular weight of the costabilizer, low solids content,...) yield less settling/creaming. Delgado et al. [33] reported that the stability towards centrifugation increased as either the surfactant concentration or the costabilizer concentration increased. Gooch et al. [109] showed that shelf stability increased with sonication time. do Amaral and Asua [60] found that the number of passes through a Manton–Gaulin homogenizer improves shelf stability. Miller et al. [29] reported that the stability of cetyl alcohol containing miniemulsions decreased as small amounts of polymer were added. Wang and Schork [22] showed that hexadecane miniemulsions presented much better shelf stability than miniemulsions stabilized with polymer. Fontenot and Schork [57] reported that miniemulsions containing higher concentrations of surfactant settled first. This effect was attributed to a lower efficiency of the sonication as surfactant concentration increases. However, the droplet size data

reported in that work showed that droplet size decreased with surfactant concentration, which is a proof against a lower efficiency of the sonication. Weiss et al. [110] also found that the Ostwald ripening of *n*-tetradecane droplets increased with surfactant concentration. These authors proposed a mass transfer mechanism in which surfactant micelles act as carriers to facilitate the transport of the water-insoluble compound between droplets.

Costabilizers also have a higher chemical potential in the small droplets and hence they are subjected to a driving force to diffuse from small to large particles. The rate of this diffusion is inversely proportional to the costabilizer water solubility. Several works confirm that miniemulsions degrade by costabilizer diffusion. Miller et al. [68] found that the droplet size (measured by CHDF) of miniemulsions containing cetyl alcohol increased with time, whereas that of miniemulsions stabilized with hexadecane remained constant. Alduncin et al. [28] investigated the feasibility of using oil soluble initiators to prevent Ostwald ripening, finding that miniemulsions degraded more rapidly as increasingly water-soluble initiators were used. Chern and Chen [32] studied the stability of styrene miniemulsions using hexadecane (HD), lauryl methacrylate (LMA), stearyl methacrylate (SMA) and cetyl alcohol (CA) as costabilizers finding that the droplet size of the miniemulsions containing the very water-insoluble HD and SMA did not change with time, whereas the droplet size increased substantially for the miniemulsions with CA and DMA.

Chern and Chen [32] also reported that a separate monomer phase was observed on top of the samples for the miniemulsions stabilized with HD and SMA. Interestingly, the monomer phase disappeared when the miniemulsions were post-stabilized with additional surfactant after the preparation step. On the other hand, no separate monomer phase was observed when a non-ionic surfactant (NP40) was used instead SLS. Landfester [111] also found that miniemulsion stability can be improved by adding more surfactant after homogenization. These results show that droplet coalescence plays an important role in destabilizing monomer miniemulsions. This has been confirmed by Katsumoto et al. [112] who studied the stability of dispersions of hexadecane in water finding that, initially, the evolution of the droplet diameter was in agreement with a diffusion-controlled mechanism of coagulation, and later Ostwald ripening was operative.

A variable that has not received much attention in literature is temperature. Ugelstad et al. [13] found that the degradation rate of styrene miniemulsions stabilized with sodium hexadecyl sulphate and hexadecanol substantially increased with temperature. Huang et al. [39] also found that the relative storage stabilities of styrene–butyl acrylate miniemulsions stabilized with SLS and HD decreased by a factor of 200 when they are stored at 80 °C compared to 20 °C. These results are extremely important because polymerizations are carried out at high temperature, and consequently the number of droplets determined at low temperature could be much higher than that in the reactor. Actually, Chern and Chen [113] showed that, for styrene miniemulsions using a nonylphenol polyethoxylate surfactant and SMA as costabilizer and the same preparation and storage conditions, the droplet size in the reactor before the start of the polymerization increased from 200 nm at a reactor temperature of 60 °C up to 650 nm when the reactor temperature was 80 °C.

Reimers and Schork [102] reported that the creaming rate of methyl methacrylate miniemulsions stabilized with poly(methyl methacrylate) depended on the molecular weight of the polymer. The minimum creaming rate corresponded to molecular weights in the range of 350 000 g/mol. Lower (33 000 g/mol) and higher (1 050 000 g/mol) molecular weights gave faster creaming rates. Surprisingly, they reported that the intermediate molecular weights yielded larger droplets than both small and large molecular weights. No clear explanation for these results was provided.

4. Polymerization of monomer miniemulsions

4.1. Particle nucleation

Droplet nucleation is a unique feature of miniemulsion polymerization and, as shown below, the reason for the wide range of applications of miniemulsion polymerization. However, in spite of its importance, it is not well understood and conflicting results have been reported leading to different theories. Thus, while some authors claim that narrow PSDs are obtained in miniemulsion polymerization [22], others report very long nucleation periods [114,115] and claim that miniemulsion intrinsically leads to broad PSD that is actually used to produce low viscosity high solids latexes [38]. Polymer particles are claimed to be one-to-one copy of the monomer droplets by some authors [71], whereas others think that only a fraction of the monomer droplets become nucleated [30,33]. This created a very confusing situation, and ‘open-to-discussion ideas’ are quoted as absolute truths. In addition to the complications inherent to any nucleation process, this situation is, in a large extent, due to the lack of reliable characterization methods for the miniemulsion droplets, and to the poor use of the methods available for characterization of polymer particles (e.g. many conclusions about nucleation mechanisms are based on the number of droplets and particles calculated from scattering measurements, and a simple error propagation calculation shows that the accuracy of these determinations is very poor). Another reason for this situation is that conclusions based on results obtained under a narrow range of experimental conditions are extrapolated to any condition without further analysis. A final reason is that many results that are in conflict with previously reported investigations are published without any reference to those investigations.

The characteristics of the miniemulsion that is charged into the reactor depend on the formulation, homogenization procedure and storage time. In general, the miniemulsion is composed of submicron monomer droplets stabilized with a surfactant against coalescence and with a costabilizer to minimize Ostwald ripening. These droplets are not equal in size but have a DSD. Depending on the amount of surfactant used in the formulation and on the homogenization procedure, micelles may be present. Assuming that a water-soluble initiator is used, particle nucleation involves the following series-parallel processes:

- (i) Radical formation in the aqueous phase by initiator decomposition (these radicals are too hydrophilic to enter into monomer droplets or micelles).
- (ii) Polymerization of the radicals in the aqueous phase to give oligomers of increasing hydrophobicity.
- (iii) Once the oligoradicals are hydrophobic enough, they can enter into monomer droplets (droplet nucleation) and micelles (micellar nucleation). They may also grow to a length that makes them insoluble in water and precipitate (homogeneous nucleation).
- (iv) In addition to droplet nucleation, monomer droplets may disappear by coalescence with other droplets and polymer particles, as well as by diffusional degradation if the costabilizer is water-soluble enough to diffuse from small to large droplets.

For practical reasons, it is important to maximize the fraction of particles generated by droplet nucleation. This fraction depends on the number of droplets and micelles and on the relative values of the rate coefficients for entry of radicals into monomer droplets and micelles, and the propagation rate in the aqueous phase. The presence of micelles depends on the amount of surfactant and the

homogenization procedure. In miniemulsion polymerizations using hexadecane, Hansen and Ugelstad [27] observed that as the intensity of the homogenization increased, the number of polymer particles initially decreased and after going through a minimum increased again. At low homogenization intensity, big droplets were formed and free surfactant formed micelles that gave particles by micellar nucleation. As homogenization intensity increased, smaller droplets were formed and more surfactant was required to stabilize these droplets, leaving less free surfactant to form micelles. The number of particles decreased because micellar nucleation decreased. At a higher homogenization intensity, micelles disappeared and formation of particles occurred by droplet nucleation. Under these conditions, increasing homogenization intensity produced more droplets, and hence the number of particles increased. Lim and Chen [41] investigated the miniemulsion polymerization of styrene using a block copolymer as surfactant and hexadecane as costabilizer finding that a significant fraction of particles were formed by micellar (and perhaps homogeneous) nucleation at high surfactant concentrations. In the miniemulsion polymerization of vinyl chloride, Saethre et al. [21] found that particles were produced by micellar nucleation when the concentration of free surfactant (taking into account the amount adsorbed on the droplets and particles) was above the CMC.

In most cases, micelles are avoided by adjusting the surfactant concentration and the homogenization conditions. Under these circumstances, the fraction of the polymer particles generated by droplet nucleation is determined by the fraction of radicals captured by the monomer droplets relative to the fraction that precipitates in the aqueous phase producing particles by homogeneous nucleation. The fraction of radicals captured by the droplets depends on the number of droplets (that can be varied as shown above) and on the rate of radical entry. For miniemulsions containing cetyl alcohol, early work showed that homogeneous nucleation was difficult to avoid in miniemulsion polymerization [27] and that this process presented a relative slow nucleation stage [30,116]. Both effects were attributed to a reduced radical absorption rate. Assuming that the number of droplets plus particles remain constant, Chamberlain et al. [116] estimated the value of the average entry rate per particle by model fitting, finding that radical entry was much slower than in the case of conventional emulsion polymerization. The slow entry rate was attributed to the interfacial complex formed by the cetyl alcohol with the surfactant and/or to the low concentration of monomer in the aqueous phase resulting from the super-swelling action of the cetyl alcohol. Unfortunately, the assumptions used made the work inconclusive. Tang et al. [99] eliminate the uncertainty associated with the number of droplets and particles by using a polystyrene seed swollen with cetyl alcohol and styrene. The monomer/polymer ratio was varied between 1.36/1 and 50/1. The conversion data were analyzed by the method developed by Asua et al. [117], and it was concluded that high swelling resulted in a decrease of both radical entry and exit rate coefficients. However, the results were not conclusive because the experiments were carried out under conditions in which the average number of radicals per particle, \bar{n} , was smaller than 0.5, and in this case, the entry and exit rate coefficients are correlated. Several experiments carried out under different conditions are required for an accurate estimation of the parameters [118–120].

Chern et al. [44] investigated the extent of the droplet nucleation by using a water-insoluble dye dissolved in the monomer droplets. Polymerizations were carried out under conditions in which no micelles were present in the system. Using stearyl methacrylate as both costabilizer and comonomer they found that, at low initiator concentrations, about 64% of the polymer particles were formed by droplet nucleation, the rest being produced by homogeneous nucleation. The fraction of polymer particles formed by droplet nucleation decreased to 34% for high initiator concentrations. Huang et al. [39] observed that increasing the amount of surfactant, but keeping its concentrations in the aqueous phase

below the CMC, increased the extent of homogeneous nucleation because the precipitating oligomers had more surfactant available for stabilization.

Polymerization in the aqueous phase is strongly influenced by the presence of hydrophilic functional monomers. Chern and Sheu [121] investigated the effect of using 2-hydroxyethyl methacrylate (HEMA) in styrene miniemulsion polymerization costabilized with SLS and long chain alkyl methacrylates. They reported that the fraction of polymer particles formed by droplet nucleation decreased by increasing the amount of HEMA, even though the total number of particles formed by droplet nucleation increased because HEMA presents some surface activity and yields a higher number of droplets. When a completely water-soluble monomer such as acrylic acid (AA) was used, Chern and Sheu [122] surprisingly observed that the extent of homogeneous nucleation decreased as the concentration of acrylic acid increased, presumably because the water solubility of the oligomers increased with the AA content. This idea was further supported by the observation that at equal molar concentrations, homogeneous nucleation was more important for methacrylic acid than for acrylic acid. Chern and Liou [123] compared the effect of the initiator type (AIBN vs. KPS) on the extent of the homogeneous nucleation finding that the oil-soluble AIBN promotes nucleation in monomer droplets whereas homogeneous nucleation predominates in the system initiated with the water-soluble KPS. Saethre et al. [21] also found that the number of particles formed by processes other than droplet nucleation increased with the water-solubility of the initiator. In addition, H_2O_2 gave less homogeneous nucleation than KPS, probably because sulfate terminated radicals have surface activity that may provide some self-stabilization to the precipitating radical.

Costabilizers are included in the formulation to preserve the identity of the monomer droplets. Both droplet coalescence and costabilizer diffusion put this objective in danger. Rodriguez et al. [34] found that a highly water-insoluble inhibitor (2,5 di-*tert*-butyl hydroquinone) dissolved in the miniemulsion droplets inhibited polymerization in the seed polymer particles that contained an oil-soluble initiator (AIBN). The inhibition was stronger at high agitation rates. This result strongly suggests that coalescence took place during polymerization. These results were analyzed by using a mathematical model [124] that considered transport by both diffusion and collision, finding that at 120 rpm 80% of the transport was by collision.

Monomer droplets can also disappear by diffusion of the costabilizer. An indirect proof of this is provided by miniemulsion polymerizations stabilized using cetyl alcohol and hexadecane. For these systems, it has been found that HD yielded higher number of particles than CA [35]. In this respect it is worth remembering that HD provides good shelf stability whereas CA miniemulsions degrade substantially as a function of time [32]. Alduncin et al. [28] investigated the ability of a series of initiators of different water solubility in stabilizing monomer droplets during miniemulsion polymerization, observing that the final PSD evolved from unimodal to bimodal as the water solubility of the initiator increased. Chern et al. [44] showed that the fraction of polymer particles formed by droplet nucleation decreased as the water solubility of the costabilizer increased. Reimers and Shork [31] found that the majority of the polymer particles were produced by processes other than droplet nucleation when several water-insoluble monomers were used as reactive costabilizers.

The final PSD depends on the interplay between all processes listed above. Miller et al. [125] performed a very detailed study of the evolution of the polymerization rate (monitored by calorimetry) and PSD (TEM) during the miniemulsion polymerization of styrene costabilized with SLS and cetyl alcohol. They found that particle nucleation occurred up to 40–60% conversion. As a consequence of the

Table 3

Dependence of number of particle on surfactant and initiator concentrations ($[\text{surfactant}]^\alpha$; $[\text{initiator}]^\beta$)

Monomer	Costabilizer	Surfactant	Initiator	Measurement particle size	α	β
Styrene [30]	Cetyl alcohol	SLS	KPS	TEM		0.37
Styrene [30]	Cetyl alcohol	SLS	AMBN	TEM		0.21
VAc/BA [126]	HD	SHS	KPS	TEM	0.25	0.80
Styrene [125]	Cetyl alcohol	SLS	KPS	TEM		0.31
Styrene [105]	HD	SLS	KPS	CHDF		0.11
Styrene [125]	CA + polymer	SLS	KPS	TEM		0
Styrene [105]	HD + polymer	SLS	KPS	CHDF		0
MMA [24]	PMMA	SLS	KPS	QELS		0
Acrylonitrile [127]	HD	SLS	V59	TEM	1.4	
VAc/MA [128]	HD	Aerosol MA	KPS			0.63
MMA [129]	HD	SLS	KPS	QELS	0.77	0.11

long nucleation periods, the latexes produced in these polymerizations were broader than in their conventional emulsion polymerization counterparts. PSDs were negatively skewed (long tails of small particles) suggesting that the rate of particle nucleation decreased with time. The amount of negative skewing of the PSD decreased with initiator concentration because the length of the nucleation period (time) decreased with initiator concentration. A few quantitative relationships giving the dependence of the number of particles on the experimental conditions (surfactant and initiator concentrations) are available (Table 3). It is worth pointing out that the variety of experimental conditions makes comparison between these correlations difficult.

Perhaps the most intriguing feature of the nucleation process in miniemulsion polymerization is the effect of the presence of small amounts of polymer in the miniemulsion droplets on both the final number of polymer particles and polymerization rate. The origin of these studies can be traced to the attempts of Tang et al. [99] to determine whether cetyl alcohol caused a decrease of the radical entry rate. These authors used a polymer seed swollen with monomer and cetyl alcohol to determine the entry rate coefficient. They concluded that the entry rate coefficient decreased significantly when the monomer/polymer ratio increased from 15/1 to 50/1. Although as discussed above the results were not conclusive, they prompted the group at Lehigh University to investigate the role of the dissolved polymer in depth.

Miller et al. [29,125,130–132] carried out styrene miniemulsion polymerizations using different costabilizers: CA, HD, CA + polymer and HD + polymer. These miniemulsion polymerizations were compared with a conventional emulsion polymerization. The stability of the miniemulsions ranked according to Eq. (17). It was found that the polymerization rate followed the following order: $R_{\text{pCA}} < R_{\text{pHD}} < R_{\text{pHD+polymer}} < R_{\text{pCA+polymer}}$. The difference in polymerization rate was due to the different number of particles nucleated in each process. Several miniemulsions stabilized with CA + polymer using different amounts of polymer were carried out, finding that only marginal gains in polymerization rate were observed for polymer contents over 0.5 wt%. In addition, it was observed that long polystyrene chains ($M_n = 193\,300$ g/mol) containing sulfate end groups performed slightly better than a short uncharged polystyrene ($M_n = 60\,300$ g/mol). The effect of initiator concentration in miniemulsion polymerization stabilized with CA and CA + 1% of polymer was investigated. It was found that in the miniemulsion polymerization stabilized with cetyl alcohol, the final number of polymer particles

increased with initiator concentration. In the miniemulsion polymerizations stabilized with CA + 1% polymer, the final number of polymer particles was not affected by the initiator concentration, but the shape of the PSD changed. It was bimodal with a peak of very small particles (10–35 nm) at low initiator concentrations and unimodal with particles larger than 30 nm at high initiator concentrations. According to Miller et al. [131], the small size particles observed at low initiator concentrations corresponded to non-initiated monomer droplets (a 20 nm ‘polymer particle’ contains the same amount of polymer as a 93 nm monomer droplet with 1 wt% of polymer). The authors attributed the enhancement in nucleation rate to the higher efficiency of the droplets containing polymer in capturing aqueous phase radicals. Possible reasons given by Miller et al. [132] for the difference in radical capture abilities of monomer droplets and monomer + polymer droplets were:

- (i) Polymer increases the viscosity of the droplets increasing the probability of the entering radicals to propagate rather than to desorb.
- (ii) Polymer chains disrupt the order of the SLS/CA condensed phase residing at the surface of the droplets destroying the barrier to radical entry.
- (iii) Polymer may provide an extra stability to the small droplets preventing them to disappear.

These hypotheses were checked by Blythe et al. [100,105,114,133] who showed that the nucleation and polymerization rate enhancement were not affected by the molecular weight of the polymer (from 39 000 to 206 000 g/mol). This result ruled out the effect of the internal viscosity on the entry efficiency. In addition, neither the number of particles nor the polymerization rate was affected by the polymer end group ($-\text{SO}_3^-$, $-\text{SO}_4^-$, H) that indicates that the enhanced droplet nucleation was not due to the disruption of the condensed phase by the polymer. Therefore, it was proposed that the dominating cause of enhanced droplet nucleation was the preservation of monomer droplets by the presence of the polymer.

In terms of the theoretical framework discussed above, the results of the miniemulsion polymerizations containing CA, HD, CA + polymer and HD + polymer can be explained as follows. Hexadecane stabilizes small monomer droplets better than cetyl alcohol because it is less water-soluble and hence is almost unaffected by Ostwald ripening. Consequently, the number of monomer droplets is higher for hexadecane stabilized miniemulsions and this leads to a higher number of particles and a higher polymerization rate. When polymer is included in a cetyl alcohol containing miniemulsion, a complex thermodynamically and kinetically based process occurs. In order to analyze this system let us consider first a miniemulsion of pure cetyl alcohol. Such a miniemulsion is affected by Ostwald ripening because of the minute water-solubility of the cetyl alcohol. If polymer is added to the CA miniemulsion, the polymer is completely insoluble in water, therefore it is confined in the droplets.

Although the swelling capacity of the polymer is limited (Fig. 5), it is still significant and the polymer will reduce the diffusion of CA from small to large droplets stabilizing the miniemulsion. In a monomer miniemulsion containing CA + polymer, the main effect of the polymer is to avoid the diffusion of the cetyl alcohol, which in turn promotes super-swelling of the droplet by monomer. Addition of polymer to miniemulsions containing hexadecane does not result in a large increase of the number of particles because Ostwald ripening almost does not affect hexadecane. Nevertheless, some enhancement was observed, as polymer was included in the hexadecane-stabilized miniemulsions. Miller et al. [130] showed that miniemulsions stabilized with cetyl alcohol plus polymer polymerized faster than those with hexadecane plus polymer. The difference may be due to the surface activity of the cetyl alcohol that

may reduce the interfacial tension allowing smaller droplets to break up or/and may provide additional protection against droplet coalescence.

Miniemulsions containing only polymer as costabilizer present an interesting behavior as they cream rapidly, but exhibit a polymerization rate between that of the cetyl alcohol miniemulsion and the cetyl alcohol plus polymer miniemulsion [130,133]. In addition, the polymerization rate is not affected by either the aging time or the molecular weight of the polymer [133]. These results suggest that polymer is able to preserve the small droplets. However, the polymer is not a good swelling agent, and the monomer/polymer ratio at equilibrium swelling is about 3/1 (vol/vol) for small droplets and about 5/1 for large droplets (see Fig. 5). This means that not only the small droplets, but also the large ones have an excess of monomer for a formulation containing 1 wt% of polymer. Therefore, monomer should diffuse out of both small and large droplets to form a separate monomer phase under equilibrium conditions. However, no monomer pooling was reported in those experiments. This means that the system stays, at least for some time, under metastable conditions. A possible reason for this is that the formation of the separate monomer phase requires the nucleation of very small droplets in which the chemical potential of the monomer is very high, and this may act as an activation energy barrier. Miller et al. [130] found that the polymerization rate of miniemulsions stabilized only with polymer was slightly faster and had a slightly higher number of polymer particles than that stabilized with hexadecane and polymer. No explanation of this result was offered and it is possible that the differences were within the experimental error.

The formation of small droplets is a requirement for the enhancement in both droplet nucleation and polymerization rate caused by the polymer. Blythe et al. [100] showed that no enhancement due to the presence of polymer was observed in miniemulsion polymerization stabilized with cetyl alcohol when low intensity of homogenization was applied (e.g. by using a less efficient shear device or using short sonication times). The reason is that the number of small droplets formed was small and their contribution to polymerization rate was negligible as compared with the large droplets that can be stabilized by the cetyl alcohol. These authors also showed that the more efficient the homogenization device the higher the number of particles and the polymerization rate.

Blythe et al. [114] showed that when the miniemulsions were costabilized with cetyl alcohol and a small amount of polymer, nucleation was extended up to almost 80% conversion. This means that long nucleation periods are not a proof of inefficient radical capture. Long nucleation processes (up to 80–90% conversion) were also observed for the styrene miniemulsion polymerization stabilized with hexadecane and hexadecane plus polystyrene [105], as well as in the miniemulsion copolymerizations of vinyl acetate–butyl acrylate and vinyl acetate–dioctyl maleate [134]. In the case of the miniemulsion stabilized with hexadecane, the final number of particles was proportional to $[\text{initiator}]^{0.11}$, whereas for miniemulsions stabilized with hexadecane plus polymer, the final N_p was independent of initiator concentration. This was taken as an indication that virtually 100% of the droplets was nucleated when the miniemulsion was stabilized with HD plus polymer. It is believed that in miniemulsions costabilized with hexadecane, the non-initialized droplets lose most of the monomer and once they are small enough, the driving force for hexadecane diffusion is large enough to force the mass transport of hexadecane from the small droplets to the large ones, and the small droplets disappear. Blythe et al. [105] found that the final number of polymer particles slightly decreased with the molecular weight of the pre-dissolved polymer because the internal viscosity of the droplets increased with the molecular weight of the polymer, and the higher the viscosity the lower the number of droplets (Eq. (8)).

Blythe et al. [135] investigated the effect of using oil-soluble initiators (2,2'-azobis(2-methylbutyronitrile),

AMBN) in miniemulsion polymerization finding that the polymerization rate of miniemulsions stabilized with CA is substantially faster than that of conventional emulsion polymerization. This result is in strong contrast with the kinetics of miniemulsions initiated with water-soluble initiators where conventional emulsion polymerization is much faster than miniemulsion polymerization [130]. These results support the idea that single unit radicals are mainly produced by initiator decomposition in the oil phase followed by desorption of one of the radicals [136,137]. Blythe et al. [135] found that the addition of a 1 wt% of polymer also led to a substantial increase of the polymerization rate for systems initiated with oil-soluble initiators. Blythe et al. [138] found that addition of a water-soluble inhibitor to a miniemulsion polymerization initiated with an oil-soluble initiator resulted in enhanced polymerization rates and, in general, increased the number of polymer particles. The same inhibitor added to a conventional emulsion polymerization initiated with an oil-soluble initiator produced lower polymerization rates.

The most attractive consequence of the investigations carried out by Miller et al. [29,130–132] and Blythe et al. [100,105,133] is the possibility of initiating all of the droplets in the miniemulsion. Several authors have reported results suggesting nucleation of all of the monomer droplets. Reimers and Schork [24] observed that in methyl methacrylate miniemulsion polymerizations using poly(methyl methacrylate) as sole costabilizer, the final number of polymer particles did not depend on initiator concentration. Bechthold and Landfester [139] reported that in the styrene miniemulsion polymerization initiated with potassium persulfate and costabilized with SLS and HD plus polymer, the final particle number was independent of initiator concentration from 8×10^{-5} to 4×10^{-4} M, but decreased at higher initiator concentrations, perhaps due to colloidal destabilization caused by the increase of ionic strength. Bechthold and Landfester [139] also reported that the number of polymer particles in miniemulsions stabilized with HD was higher than that in miniemulsions stabilized with HD plus polymer. In addition, they found that increasing polymer concentration from 1 to 2% led to a significant decrease in the number of polymer particles. This is in contradiction with the results reported by Miller et al. [130], and no explanation was offered. A possible reason for these results is that the number of monomer droplets may decrease as the polymer content increases because of the augmentation of the internal viscosity (Eq. (8)). This effect is likely to be more apparent in the case of using sonication (Bechthold and Landfester [139]) than a high pressure homogenizer (Miller et al. [130]). It is worth pointing out that the use of polymer as costabilizer does not guarantee that most droplets are nucleated or that droplet nucleation is the sole nucleation mechanism. Thus, Gooch et al. [109] attempted producing hybrid polyurethane–acrylic latex particles by miniemulsion polymerization using the polyurethane as costabilizer. A decrease of 12–29% (depending on experimental conditions) in the particle size along the reaction was reported. This corresponds to a variation on the average particle volume of 40–114%, which cannot be caused by the different densities of monomer and polymer and should be due to formation of new particles, presumably by homogeneous nucleation.

Recently, Landfester et al. [71] have coined the term ‘one-to-one’ copy for a miniemulsion polymerization process in which all monomer droplets are nucleated, and the final PSD is the same as the original DSD. Based on a combination of SANS, conductivity and surface tension measurements, they claimed that a one-to-one copy occurred in the miniemulsion polymerization of styrene stabilized with hexadecane and SLS and initiated with AIBN. A one-to-one copy process would require (i) a very fast nucleation step, (ii) polymerization rate much faster than the monomer mass transport rate among particles, and (iii) negligible droplet–droplet and droplet–particle coalescence, and particle–particle coagulation. In addition, some narrowing of the PSD is produced if the average number of radicals per

particle is equal to or slightly higher than 0.5 [27]. However, it is doubtful that these requirements would be fulfilled under the experimental conditions used by Landfester et al. [71]. Thus, long nucleation periods have been systematically reported in works analyzing the PSD by TEM in miniemulsions initiated with oil-soluble initiators [28,135]. In addition, for the same miniemulsion polymerization system with higher initiator concentrations and higher polymerization temperatures, it has been reported that the PSD as measured by TEM varied continuously along the reaction [28] and that the polymerization took a rather long time to reach high conversion [40], namely, that it is unlikely that the mass transfer rate was slower than the polymerization rate. One wonders if the scattering technique used by Landfester et al. [71] was accurate enough to determine the actual particle and DSDs.

The concept of a ‘one-to-one’ copy is appealing but remains to be demonstrated. In addition, it is misleading and it is in some cases taken as a feature of miniemulsion polymerization, instead of a possibility that might be reached if the experimental conditions that meet some very demanding requirements (see above) are found. Statements such as “Since nucleation is in the droplets themselves, the droplet and latex particle diameters should not differ” [140], “Due to the fact that the polymerization time is usually shorter than the growth of the droplets by collisions, the polymerization in carefully prepared miniemulsions results in latex particles which have about the same size as the initial droplets” [141], and “Polymerization of the droplets leads to particles that ideally keep their size” [142] are being used to describe inherent properties of the miniemulsion polymerization that it does not possess. In some cases, this pre-conception has influenced data analysis. Thus, Gooch et al. [109] analyzing the evolution of the particle size in the miniemulsion polymerizations carried out to produce hybrid polyurethane–acrylic latex using the polyurethane as costabilizer stated “As described above, the dominant nucleation mechanism in miniemulsion polymerization is droplet nucleation. Consequently, the final latex particle size will be similar to the initial monomer droplet size. ‘ure 1 shows this feature in the current system. The particle size decreased slightly during polymerization. This can be attributed to the decrease of particle density, because polymer density is higher than that of the monomers”. However, the reported decrease in particle size along the reaction was 12–29% (depending on experimental conditions). This corresponds to a variation on the average particle volume of 40–114%, which cannot be caused by the different densities of acrylic monomers and polymers. The one-to-one copy is a desirable feature of miniemulsion polymerization, but the conditions required to achieve this goal seem to be very difficult to attain in practice. Consequently, one should be cautious about using this concept to analyze miniemulsion data.

Industrial implementation of polymerization in dispersed media involves mostly semicontinuous processes because these systems are a versatile way of controlling both the quality of the product and the temperature in the reactor. In spite of the importance of the semicontinuous processes, only a few works have been carried out to investigate droplet nucleation in semicontinuous operations. In seeded semicontinuous polymerizations, Tang et al. [26] found that almost no new particles were produced when neat monomer addition was used, but substantial secondary nucleation leading to bimodal broad PSDs was observed when a monomer miniemulsion was fed. The final number of polymer particles, N_p , was not significantly affected by the miniemulsion feed rate at high seed contents. When the amount of seed was small, N_p increased with the miniemulsion feed rate. In the semicontinuous copolymerization of styrene/2-ethylhexyl acrylate/methacrylic acid, Masa et al. [37] reported that the extent of the secondary nucleation that occurred during the feed period was greater for miniemulsion feed than for a pre-emulsified feed. In the semicontinuous miniemulsion polymerization of vinyl acetate and dioctyl maleate, Wu and Schork [134] found that polymer particles are continuously nucleated through the

process. Continuous nucleation was also observed in the conventional semicontinuous emulsion polymerization. These results show that typically, the presence of submicron monomer droplets leads to particle nucleation.

4.2. Particle growth

In miniemulsion homopolymerization, once the polymer particles are nucleated, the processes controlling particle growth are the same as in a conventional emulsion polymerization. Some retention of the monomer in the non-nucleated droplets may be expected leading to a slight reduction of the concentration of the monomer in the polymer particles, and hence to a somehow lower polymerization rate. The situation is more complex in miniemulsion copolymerization because two or more monomers are involved and the partitioning of the monomers between the phases of the system may lead to variations in the copolymer composition.

In the batch miniemulsion copolymerization of vinyl acetate and butyl acrylate, Delgado et al. [33,143] found that for the same overall conversion, the polymer formed by the miniemulsion process contained less VAc units than that formed through conventional emulsion polymerization. Simulations showed that the presence of hexadecane increased the butyl acrylate/vinyl acetate monomer ratio in the polymer particles [92].

In the semicontinuous copolymerization of styrene/2-ethylhexyl acrylate/methacrylic acid, Masa et al. [37] reported that the concentration of carboxylic groups at the surface of the polymer particles was higher for miniemulsion polymerization than for conventional emulsion polymerization. This result was attributed to the higher polymerization rate of the conventional process that maintained the system under more starved conditions, minimizing migration of the polymer chains containing carboxylic groups towards the surface of the polymer particle. Another reason may be the greater hydrophobic character of the interior of the miniemulsion particles that brought the carboxylic acid groups to the surface of the particles.

Kitzmilller et al. [49] studied the miniemulsion copolymerization of VAc and vinyl 2-ethyl hexanoate (V2EH) stabilized with hexadecane and a polymerizable surfactant. It is stated that a more uniform incorporation of V2EH should be achieved in miniemulsion polymerization as compared with the conventional process, but no data were provided.

Samer and Schork [144] reported that the incorporation of 2-ethylhexyl acrylate (2EHA) in a MMA/2EHA copolymer was higher when the copolymer was produced by miniemulsion copolymerization than when the conventional emulsion process was used. It was thought that 2EHA was affected by diffusional limitations in the conventional emulsion polymerization whereas droplet nucleation minimized the need for 2EHA mass transport in miniemulsion polymerization. No difference in the incorporation of 2EHA between conventional emulsion polymerization and miniemulsion polymerization was observed in continuous stirred tank reactors (CSTR).

Reimers and Schork [31] studied the evolution of copolymer composition along the process in both miniemulsion and conventional emulsion copolymerization of MMA with several monomers of different water-solubility. It was found that, for monomers with a sufficient water-solubility, the polymerization process did not affect the copolymer composition. On the other hand, the incorporation of the water-insoluble monomers into the copolymer was better in miniemulsion polymerization than in the conventional emulsion process, because droplet nucleation minimized the need of monomer transport. For some comonomers (vinyl decanoate and vinyl stearate), it was found that they were incorporated into the

mini-emulsion copolymer in quantities higher than those predicted by the Mayo–Lewis equation under bulk conditions. Micelles were claimed to be responsible for retaining a fraction of MMA outside the polymerization loci, but the existence of micelles was not demonstrated.

Wu and Schork [134] investigated the effect of the batch polymerization process (mini-emulsion vs. conventional emulsion) on the copolymer composition for three comonomer systems of widely different reactivity ratios and water solubilities: vinyl acetate–butyl acrylate (VAc–BA), vinyl acetate–dioctyl maleate (VAc–DOM), and vinyl acetate–*n*-methylol acrylamide (VAc–NMA). BA and NMA are much more reactive than VAc, and DOM is more reactive than VAc. Water-solubilities ranged as $NMA > VAc > BA > DOM$, NMA being very water-soluble. For the VAc–BA system, it was found that BA copolymer composition was initially richer in BA than the feed and that this effect was slightly more pronounced for the mini-emulsion process, which suggests that BA was slightly affected by diffusional limitations. In the mini-emulsion copolymerization of VAc–DOM, in agreement with the reactivity ratios, DOM was preferentially incorporated into the copolymer. However, in spite of the higher reactivity ratio of DOM, the copolymer was richer in VAc in the conventional emulsion because DOM could not diffuse from the monomer droplets to polymer particles. For the VAc–NMA comonomer system, in agreement with the reactivity ratios, NMA was preferentially incorporated into the copolymer, the NMA content of the mini-emulsion copolymer being higher than that of the conventional process. The reason was that in the conventional process a large amount of the NMA stayed in the aqueous phase, whereas in the mini-emulsion polymerization the hexadecane brought a larger fraction of NMA into the polymer particles.

Wu and Schork [134] also compared mini-emulsion polymerization and conventional emulsion polymerization carried out in a semicontinuous reactor. The same comonomer systems described above were used. They found that the water-insoluble monomers (BA and DOM) were incorporated into the copolymer in an easier manner when a mini-emulsion feed was used, but no effect was observed for the VAc–NMA system.

In homopolymerization, the molecular weights produced by mini-emulsion polymerization are the same as in conventional emulsion polymerization when compartmentalization has no effect on MWD ($\bar{n} \ll 0.5$ or $\bar{n} \gg 0.5$) [145] or when similar particle sizes are obtained. Under conditions in which compartmentalization affects MWD, mini-emulsion polymerization may lead to molecular weights different than those of the conventional process. Thus, using oil-soluble initiators, Alduncin and Asua [40] found that the molecular weights obtained in the styrene mini-emulsion polymerization were well fitted with a bulk polymerization model, and they were substantially smaller than those obtained in conventional emulsion polymerization. In mini-emulsion polymerization large particles were obtained and hence ($\bar{n} \gg 0.5$). However, in the conventional process small particles were produced, and compartmentalization led to an increase of molecular weights.

In mini-emulsion copolymerization, the partitioning of the comonomers may affect molecular weights. For several comonomer systems, and in both batch and semicontinuous operations, Wu and Schork [134] reported slightly higher molecular weights for conventional emulsion polymerization than for mini-emulsion polymerization.

Mini-emulsion feed can also be advantageously used in on-line control of the MWD. The MWD is often controlled using mercaptans as chain transfer agents. Mercaptans have offensive odors, and hence long chain mercaptans having a low vapor pressure are used. However, the longer the mercaptan chain the lower the water-solubility and the more difficult to transport it to the polymerization loci. Vicente et al. [146] showed that the diffusional limitations to the transport of the chain transfer agent from the

feed entering the reactor to the polymer particles can be minimized by using a miniemulsion feed containing the mercaptan. The reason is that the rate-determining step in the mass transfer is located at the droplet–water interface, and the tiny miniemulsion droplets have a very large surface area.

4.3. Mathematical modeling

Chamberlain et al. [116] were the first to develop a model for the batch miniemulsion polymerization of styrene by considering that the number of monomer droplets plus polymer particles was equal to the number of initial droplets. Chen et al. [147] developed a model for a continuous miniemulsion polymerization by considering that the system may be represented by a combination of suspension and emulsion polymerizations. No comparison with experimental data was presented. Delgado et al. [92] developed a model for a batch miniemulsion copolymerization. The model considered that both droplets and particles were monodisperse, and droplets could disappear by radical entry, and droplet–droplet and droplet–particle coalescence. Monomer partitioning was considered to be affected by the presence of costabilizer and ruled by mass transfer equations. Limited comparison of the model predictions with experimental data was performed showing that the model was able to account for the different evolutions of copolymer composition in miniemulsion and conventional emulsion polymerization. The model was also used to analyze interparticle monomer transport in miniemulsions [93].

Delgado's model did not consider the transport of water-insoluble compounds due to coalescence and failed accounting for the effect observed using a highly water-insoluble inhibitor in the miniemulsion copolymerization of styrene and methyl methacrylate [34]. Asua et al. [124] were able to account for these experimental finding by using an extension of Delgado's model in which mass transport of the costabilizer by collision and formation of particles by homogeneous nucleation were considered. Rodriguez et al. [94] developed a model for the batch miniemulsion polymerization initiated with oil-soluble initiators. Fontenot and Schork [148,149] considered both droplet and micellar nucleation. The model was able to fit the effect of the initiator concentration on the number of polymer particles and, for some experimental conditions the evolution of the monomer conversion. Samer and Schork [150] extended Fontenot's model to miniemulsion polymerization in CSTRs being able to partially fit experimental data collected in the miniemulsion polymerization of methyl methacrylate. The main limitation of all published models is that DSD (and PSD) is not considered, even though it has been demonstrated that it is a major factor affecting miniemulsion polymerization.

4.4. Comparison between latexes produced by miniemulsion polymerization and by conventional emulsion polymerization

Masa et al. [37] found that the latexes produced by miniemulsion polymerization had lower viscosities than those obtained by conventional emulsion polymerization, the reason being the broader PSD. These authors also found that the miniemulsion latexes presented better salt stability than the conventional latexes. The difference was attributed to the broader PSD of the miniemulsion latexes and to the different distribution of the methacrylic acid (miniemulsion latexes had a lower fraction of MAA buried inside the polymer particles). López de Arbina and Asua [36] reported that the freeze–thaw stability of miniemulsion latexes improved as solids content decreased, and was better for latexes stabilized with non-ionic surfactants as compared with ionic stabilization, but no comparison with conventional latexes was made. Rodrigues and Schork [151] investigated the shear stability of latexes of similar size produced by

mini-emulsion and conventional emulsion polymerization. It was found that mini-emulsion latexes were more stable than conventional ones. It was speculated that the difference was due to the presence of a small fraction of large particles in the conventional latex. The range of particle sizes achievable by mini-emulsion polymerization seems to be more limited than that using conventional emulsion polymerization because high solids content latexes with small particle size are difficult to obtain, although some progress has been reported [152].

5. Applications

For quite a long time, mini-emulsion polymerization remained for the most part as a scientific curiosity, kept alive by the determination of Professor El-Aasser, but in the last few years many of new applications have been discovered. These applications include:

- (i) production of high solids low viscosity latexes,
- (ii) continuous polymerization reactors,
- (iii) controlled radical polymerization (CRP) in dispersed media,
- (iv) catalytic polymerization,
- (v) encapsulation of inorganic solids,
- (vi) incorporation of hydrophobic monomers,
- (vii) hybrid polymer particles,
- (viii) mini-emulsion polymerization in non-aqueous media,
- (ix) anionic polymerization,
- (x) step polymerization in aqueous dispersed media,
- (xi) production of low-molecular weight polymers in dispersed media, and
- (xii) latexes with special particle morphology.

All these applications take advantage of the droplet nucleation mechanism occurring in mini-emulsion polymerization.

5.1. Production of high solids low viscosity latexes

High solids content latexes offer numerous advantages for most commercial applications, e.g. lower shipping costs and less water to be removed. In practice, the solids content of a latex is limited by its viscosity. For a monodisperse latex, viscosity approaches infinity as the volume fraction of the polymer particles approaches 0.64. On the other hand, polydisperse latexes show a lower viscosity, because the small particles fit within the voids of the array of the big particles. Polydispersity is often found in mini-emulsion polymerization. In batch reactors, the long nucleation periods typical of mini-emulsion polymerization, yield broad PSDs [114,115]. In semicontinuous reactors, Tang et al. [26] showed that droplet nucleation took place continuously when mini-emulsion feed was used. Masa et al. [37] compared the viscosities of 55 wt% solids styrene–2 ethyl hexyl acrylate–methacrylic acid latexes produced by mini-emulsion polymerization with those obtained through conventional emulsion polymerization finding the viscosities of the neutralized latexes were 4.5 Pa s for the emulsion latex and only 0.7 Pa s for the mini-emulsion latex. This prompted Unzué and Asua [38] to explore the possibilities of mini-emulsion polymerization to prepare high solids content latexes of low viscosity. A 65 wt% solids content latex of

low viscosity (0.44 Pa s) was obtained by means of the semicontinuous miniemulsion terpolymerization of methyl methacrylate, butyl acrylate and vinyl acetate using a mixed surfactant system and hexadecane (2 wt% based on monomers) as costabilizer.

Miniemulsions were used for both the initial charge and the feed. It was found that the distribution of the monomer between the initial charge and the feed was the key process variable. When a high solids content miniemulsion (>55 wt%) was used as the initial charge, coagulum was formed during the batch polymerization of the initial charge, whereas when a low solids content initial charge was employed, the solids content of the feed was excessive, leading to unmanageable viscosities. A compromise between these situations was achieved using a 55 wt% solids initial charge and a 66.1 wt% solids content feed. Leiza et al. [153] used a two-stage polymerization process to obtain high solids content latexes with a low amount of surfactant (SLS). The first stage was a seeded semicontinuous miniemulsion polymerization. The latex obtained in the first stage was used as the initial charge for the second stage, in which a pre-emulsion of monomer was used as seed. A 61 wt% solids latex with only a 0.5 wt% based on monomer of SLS was obtained. Dames et al. [154] disclosed a procedure to prepare latexes with bimodal PSDs by using a seed latex that is polymerized in a semicontinuous process and then adding a miniemulsion towards the end of the process.

5.2. Continuous polymerization reactors

Continuous reactor processes for the manufacture of selected latex products have been used since the 1940s [155,156]. In recent years, the latex industry is facing a steady increase in the price of monomer that cannot be transferred to the customers; consequently, the profit margins are shrinking. Therefore, there is a great need to reduce operation costs, and a way of achieving this is through process intensification. This can be achieved by improving the thermal characteristics of the batch reactors, e.g. by adding an external cooling circuit [157], and by switching from batch to continuous processes.

In principle, continuous processes offer the advantage of a uniform quality of the product. However, this is not often the case for conventional emulsion polymerization carried out in CSTRs [158–161] and in loop reactors [162,163], in which significant oscillations of both monomer conversion and PSD are observed. The oscillatory behavior is due to the role of the surfactant in particle nucleation. At the beginning of the process, a large number of small polymer particles is formed, their number being controlled by the amount of surfactant available in the system. These polymer particles grow by polymerization, and hence their surface area increases, depleting the aqueous phase of surfactant. Therefore, new particles are not formed and, as the reaction mixture is continuously withdrawn from the reactor, the number of particles decreases. After some time, this process counteracts the increase in size of the particles and the total surface area of the particles decreases leaving surfactant free, which can stabilize new particles starting a new oscillating cycle. This phenomenon is more acute for low surfactant concentrations and for polymerizing systems in which the volumetric growth rate of the polymer particles is strongly non-linear with particle diameter (usually systems with high desorption rates [164]). Barnett and Schork [165] reported a case in which the miniemulsion polymerization of MMA in a CSTR did not show oscillations whereas the conventional emulsion polymerization exhibited decaying oscillatory transients. No mechanistic explanation for this result was provided. Miniemulsion polymerization seemed to result in a higher number of particles and higher monomer conversion than the conventional process, although the authors pointed out that errors associated with counting particles in the TEM pictures might make the difference in particle number insignificant.

Aizpurua et al. [166] investigated the miniemulsion polymerization of vinyl acetate in a CSTR. This is a more stringent test than the miniemulsion polymerization of styrene because vinyl acetate gives a high radical desorption rate due to its large monomer chain transfer rate and high water-solubility. Consequently the system is prone to oscillate [164]. In miniemulsion polymerizations of vinyl acetate stabilized with SLS and using hexadecane as costabilizer, it was found [166] that at low surfactant concentrations, the particle size of the conventional emulsion showed severe oscillations whereas that of the miniemulsion was constant. In addition, the particle size of the miniemulsion was smaller, namely, the number of polymer particles higher. A higher monomer conversion was achieved in miniemulsion polymerization, likely due to the higher N_p . At high surfactant concentrations, neither the conventional process nor the miniemulsion polymerization presented oscillations and no differences in both the number of polymer particles and monomer conversion was observed between miniemulsion and conventional emulsion polymerization of vinyl acetate. The sustained oscillations of the particle diameter at low surfactant concentration found in the emulsion polymerization resulted from intermittent nucleation occurring through the processes described above. The reason for the absence of oscillations in miniemulsion polymerization is that a stable miniemulsion was continuously fed into the reactor. In the reactor, some of the droplets are nucleated and others may leave the reactor without being entered by a radical. Under these circumstances, the total interfacial surface area of the system was quite constant throughout the process preventing oscillations of the free surfactant level.

At higher surfactant concentrations, the conventional emulsion polymerization system never became depleted of free surfactant and hence an almost constant nucleation rate was obtained, maintaining the number of polymer particles in the reactor constant. Insufficient data about the miniemulsion process are available, but it may be speculated that in the experiments carried out with high surfactant concentrations, the miniemulsion feed contained an excess of free surfactant forming micelles. As explained above, the existence of micelles depends on both the homogenization device used and the surfactant concentration. Aizpurua et al. [166] produced the miniemulsion by passing the feed through a sonication cell before entering into the reactor. The efficiency of this homogenization device is limited and depends on the flow rate (residence time in the cell) used. Therefore, the droplet size cannot be reduced below a given level irrespective of the amount of surfactant present. The efficiency of the homogenization determines a maximum surface area that can be created in the sonicator cell, and as the amount of surfactant used was in large excess to cover this area, many micelles were fed into the reactor.

Aizpurua and Barandiaran [145] presented a detailed comparison between miniemulsion and conventional emulsion polymerization of vinyl acetate in a CSTR under a wide range of experimental conditions. It was found that miniemulsion polymerization gave broad unimodal PSDs with a shape similar to that of the residence time distribution. This is in agreement with a continuous nucleation of the monomer droplets. On the other hand, the conventional process led to a multimodal PSD typical of a system with intermittent nucleation [158,160,162,163]. Except for very high concentrations of surfactant that are likely unacceptable because they would impart a high water-sensitivity to the latex film, miniemulsions resulted in a higher number of particles and polymerization rate than the conventional process. The dependencies of N_p and R_p with respect to initiator and surfactant concentrations were:

Conventional emulsion polymerization:

$$N_p = [S]^{0.7} [I]^{0.03} \quad (19)$$

$$R_p = [S]^{0.16-0.20} [I]^{1.3-1.6} \quad (20)$$

Miniemulsion polymerization:

$$N_p = [S]^{0.25} [I]^{0.22-0.4} \quad (21)$$

$$R_p = [S]^{0.16-0.25} [I]^{0.7-1.0} \quad (22)$$

On the other hand, miniemulsion polymerization was more robust than the conventional process with respect to the start-up procedure. Aizpurua et al. [167] also investigated the feasibility of high solids content (60 wt%) miniemulsion polymerizations in a CSTR. It was found that stable operation can be achieved by using different costabilizers including hexadecane, poly(vinyl acetate) and poly(styrene).

Tubular reactors present, in principle, many advantages for conducting continuous polymerization reactions in dispersed media, but phase separation precludes their use in conventional emulsion polymerization. Miniemulsions have a much better shelf stability than conventional emulsions, and hence there is some hope that they can be implemented in tubular reactors. Promising results have been recently reported by Durant [168] and Ouzineb et al. [169].

5.3. Controlled radical polymerization in dispersed media

In the early 1990s free radical polymerization was considered to be a mature technology in which there was little more to be discovered. CRP has rejuvenated free radical polymerization making accessible a wide range of polymer architectures including narrow molecular weight polymers, multiblock copolymers, star polymers, etc. [170]. Three well-established CRP techniques are available: (i) stable free radical polymerization (SFRP) [171,172], (ii) atom transfer radical polymerization (ATRP) [173], and (iii) reversible addition–fragmentation chain transfer (RAFT) [174] along with other degenerative chain transfer processes. A comparison between these methods can be found in Ref. [175].

The majority of the work performed in CRP has carried out in bulk and solution polymerization. However, these processes are not well suited for large-scale operations and attention has turned to developing polymerization processes in dispersed systems. In order to be successful, the polymerization process should meet the following requirements [176,177]:

- (i) Stable high solids latexes should be achieved in a wide range of experimental conditions.
- (ii) The process has to be compatible with a variety of monomers.
- (iii) High monomer conversion (close to 100%) in short process times (typically less than 6 h) should be achieved.
- (iv) The living character should be preserved.
- (v) High molecular weights should be attainable.

5.3.1. Effect of compartmentalization

Both the polymerization rate and the molecular weights of a regular free radical polymerization are higher in a dispersed system than in a bulk polymerization. The reason is that in the dispersed system the

radicals confined within one polymer particle cannot terminate with the radicals in other particles. This effect is known as compartmentalization. The key aspect of CRP is to minimize bimolecular termination of radicals, therefore one wonders if compartmentalization may be of some help in CRP. Charleux [178] showed by simulation that for nitroxide-mediated SFRP, particles smaller than 50–100 nm in diameter present some degree of compartmentalization leading to faster polymerization rates but broad MWDs. It is worth pointing out that these conclusions were obtained by assuming that the nitroxide radicals do not partition between the particles and the aqueous phase, but this has been demonstrated not to be the case [179]. Based on the characteristic time of the different processes, Butté et al. [180] concluded that neither SFRP nor ATRP may benefit from compartmentalization, and that only RAFT or other degenerative transfer processes may gain from compartmentalization. In a series of miniemulsion polymerizations of styrene in batch using several RAFT agents, Butté et al. [181] reported that quite high monomer conversions (67–90%) could be achieved in relatively short process times (about 2 h), but only a limited control of the MWD was achieved (PI: 1.36–2). Two possible causes for these high PI were identified: one due to the presence in the RAFT agent of a fraction of dead chains unable to restart, and the other due to the possibility of having particles with different concentration of RAFT agent because of the different nucleation times of the droplets.

5.3.2. Stable free radical polymerization

Conventional emulsion polymerization was used in the first attempts to perform SFRP in dispersed systems. However, only very little success was reported. Bon et al. [182] were able to apply the SFRP process only in seeded emulsion polymerization by using preformed polymer particles. Marestin et al. [183] studied the emulsion polymerization of styrene obtaining latexes with a maximum 5% solids and low conversions. Conventional emulsion polymerization is not adequate for SFRP because the stable free radicals used in this process are rather water-insoluble, and they are located mainly in the monomer droplets at the beginning of the process. When polymerization starts, polymer particles are formed by homogeneous nucleation and micellar nucleation. These particles become the main polymerization loci, and as the stable free radical cannot diffuse quickly enough from the monomer droplets, considerable polymer is formed under non-controlled conditions.

Prodpran et al. [184,185] and MacLeod et al. [176] realized that this limitation could be overcome by using miniemulsion polymerization because droplet nucleation minimizes the need of transport of the stable free radical to the polymerization loci, and successfully implemented nitroxide-mediated SFRP in miniemulsion processes. Prodpran et al. [184,185] used 2,2 tetramethyl-1-piperidinyloxy nitroxide (TEMPO) as the stable free radical in polymerizations carried out at 125 °C using an oil-soluble initiator (benzoyl peroxide), an anionic surfactant (Dowfax 8390), and hexadecane as costabilizer. Stable polystyrene latexes with 20% solids and PI of 1.3–1.6 were obtained. It was observed that PI continuously increased during the process presumably due to continuous generation of free radicals by autothermal initiation of styrene. A TEMPO/BPO molar ratio of 3.0 was needed to counteract this process. The evolution of the number of particles (N_p) with conversion showed an increase in all experiments, which was attributed to the thermal initiation. In the presence of TEMPO, N_p was much lower due to the diminished contribution of the radicals formed by thermal initiation.

MacLeod et al. [176] were able to produce stable 20% solids polystyrene latexes by miniemulsion polymerization using TEMPO, hexadecane, a water-soluble initiator (potassium persulfate) and an anionic surfactant (sodium dodecylbenzenesulfonic acid). Polymerizations carried out at 135 °C with a TEMPO/KPS molar ratio of 2.9/1 yielded a polymer of PI = 1.1 and $M_n = 14\,000$ g/mol in 6 h.

Monomer conversion was limited to 87%. In an attempt to increase the final conversion, these authors [177] used a higher temperature (145 °C) and longer reaction times but monomer conversion was not significantly improved and PI increased because a large number of short chains were formed. The authors stressed that no nitroxide radical scavenger, such as camphorsulfonic acid (often used in bulk polymerization to destroy the excess of nitroxide radicals that builds up as a result of the termination of 'regular' radicals), is needed to enable the miniemulsion polymerization to proceed at a fast rate. The reason was assumed to be the partitioning of nitroxide radicals between the oil and aqueous phases. The partition coefficient for TEMPO at 135 °C is 528 [179], which, for a 20% solids latex, means that only one out of 125 TEMPO molecules is in the aqueous phase. This does not seem to be enough for a significant reduction of the concentration of nitroxide radicals in the polymer particles, and a dynamic sink for nitroxide radicals in the aqueous phase would be required, e.g. reaction with the persulfate radicals. On the other hand, Prodpran et al. [185] reported that the rate of polymerization in bulk was found to be faster than that in miniemulsion. This result, which seems to be in conflict with the discussion above, was attributed to the segregation of monomer in discrete droplets and the diffusion of active species to the aqueous phase, but these thoughts were not elaborated further. It is worth mentioning that 6–7 wt% of surfactant based on monomer was used in those works [176,184,185]. This is a very high amount for 20% solids latexes but this issue was not discussed in those reports.

Pan et al. [186] studied the miniemulsion polymerization of styrene using TEMPO-terminated oligomers (TTOPS, $M_n = 7000$ g/mol; PI = 1.24) as a macroinitiator species to initiate the polymerization at 125 °C. The MWD of the polymer formed was not narrow (PI = 1.76 for 5% of TTOPS and 76% monomer conversion; PI = 1.86 for 20% of TTOPS and 77.4% conversion). In addition, the PI increased with monomer conversion due to the autothermal generation of radicals. M_n decreased with the amount of TTOPS and the number of polymer chains was higher than the number of TTOPS molecules because of both termination and thermal initiation. Broad PSDs were observed. The broadness of the PSD yielded poor reproducibility of the measurements even though more than 4000 particles were counted from the TEM images. The number of particles increased after 50% conversion when TTOPS was used, whereas it was roughly constant in the absence of TTOPS. The mechanism of the nucleation process has yet to be determined. Keoshkerian et al. [177] also studied the miniemulsion polymerization of styrene initiated with 5 wt% TEMPO-terminated polystyrene oligomers ($M_n = 1500$ – 2500 , PI = 1.25) at 135 °C, finding that this process yielded almost complete monomer conversion (>99.5%) and narrow MWD ($M_n = 18\,800$, PI = 1.15) in 6 h. It is speculated that this was because all monomer droplets were nucleated, but the number of particles was not reported. One wonders if the different temperatures used by Pan et al. [186] (125 °C) and Keoshkerian et al. [177] (135 °C) may account for the differences in monomer conversion and broadness of the MWD. Keoshkerian et al. [177] were able to produce block copolymers by chain extension with *n*-butyl acrylate. The M_n of the product was 34 500 with a PI of 1.18, and a conversion of BA of 99.4%. This is interesting because polymerization of acrylates with TEMPO to high conversion has proven problematic over the years [187]. Controlled miniemulsion homopolymerization of butyl acrylate using different nitroxides has been reported recently [188].

One of the drawbacks of using TEMPO is that high temperatures, and consequently pressures above atmospheric, should be employed. Farcet et al. [189] studied the miniemulsion polymerization of styrene using the *N-tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (SG1) that because of its high equilibrium constant of activation–deactivation can be used at lower temperatures than TEMPO [190,191]. Stable 25 wt% latexes were obtained at 90 °C using hexadecane and polystyrene ($M_n = 330\,000$ g/mol) as costabilizers and SLS as surfactant. A redox initiator system ($K_2S_2O_8/Na_2S_2O_5$)

was used presumably in an attempt to reduce the period of radical generation. SG1 is rather water-soluble (partition coefficient = 180–450) and reacts with the radicals formed in the aqueous phase retarding the growth of these oligomers. As a minimum length is required for the oligomers to become hydrophobic enough to enter into the monomer droplets, an inhibition period that increased with the SG1 concentration was observed. In order to minimize the inhibition period, a low concentration of SG1 ($\text{SG1}/\text{K}_2\text{S}_2\text{O}_8 = 1.2$) was used. This resulted in a high polymerization rate but in a poorer molecular weight control (PI close to 1.5). It was found that pH plays a critical role in the efficiency of SG1 with an optimal range of pH 3–6.5. At a lower pH, SG1 reacts very fast with O-centered and S-centered primary radicals and at a higher pH the nitroxide radical is too stable and stops polymerization. The ‘livingness’ of the polymer chains was demonstrated by *in situ* chain extension. PSDs were broad but no study on the effect of process variables on the PSD was performed.

The drawbacks presented by SG1 can be overcome by using SG1-based alkoxyamine derivatives [192]. Stable 21% solids poly(butyl acrylate) latexes of relatively narrow MWD (PI = 1.2–1.4) were produced by miniemulsion polymerization using a SG1-based alkoxyamine derived from methyl acrylate as initiator plus a 2.5 mol% excess of free SG1. The reaction was carried at 115 °C and no reason for the use of such a high temperature was given. The PSD was broad and not reproducible with an average size in the range of 390–460 nm. The process was quite rapid reaching 80% conversion after 6.5 h. Extension of p(BA) with styrene was possible and it is reported that no pure p(BA) homopolymer chains were present in the final product. However, this seems to be in conflict with the broadness of the p(BA) MWD (PI = 1.4).

5.3.3. Atom transfer radical polymerization

ATRP employs the activation of an alkyl halide by a transition metal catalyst to form a radical, which can initiate polymerization. The growing polymeric radical is deactivated by reaction with the transition metal halide formed in the activation step. Through this activation–deactivation cycle, each polymer chain grows nearly at the same rate [193–195]. Bimolecular termination is minimized by maintaining a small concentration of active radicals. In the absence of added initiator this naturally resulted from the persistent radical effect [196].

Matyjaszewski et al. [197] showed that to successfully carry out an ATRP miniemulsion polymerization, the catalyst should be stable to homogenization (sonication in their work) and should be rather hydrophobic in order to minimize partitioning into the aqueous phase, which would prevent the deactivation of the radicals, leading to a poor control of the livingness of the radicals. In addition, ionic surfactants were reported to prevent good control of the polymer formed. It was speculated that some type of interaction of the ionic surfactant with the Cu(II)–Br catalyst existed, which renders the catalyst unable to deactivate the growing polymer chain. Non-ionic surfactants did not seem to interfere with the ATRP process. Using Brij 98 (a non-ionic surfactant with 20 poly(ethylene oxide) groups and a C18 hydrophobic chain), a 50 wt% solids stable latex of well defined poly(butyl methacrylate) ($M_n = 23\,600$, PI = 1.16) was obtained. 83% monomer conversion was reached in 2 h and relatively large amount of surfactant was used (10 wt% based on monomer). Lower solids contents required less surfactant. Large particle sizes are reported (4 μm). The particle size may be reduced ($d_p = 250$ nm) with still relatively narrow MWDs (PI = 1.3–1.4) by using a conventional radical initiator in the presence of the ATRP catalyst (reverse ATRP). The system performed equally well over a broad range of temperatures (70–90 °C).

It has been found that catalyst partitioning is monomer dependent. Thus, styrene retained 92% of the

original Cu(II) salt in the organic phase, while for butyl methacrylate only 56% remained in the organic phase. The polymerization of styrene is further retarded by this effect. The effect of catalyst partitioning was further investigated by Matyjaszewski et al. [198] in the reverse ATRP miniemulsion. It was found that the catalyst, initially present in the aqueous phase because of the partitioning, diffused to the polymer particles as the catalyst present in the polymer particles reacted with the growing radicals. For the catalyst used, $\text{CuBr}_2/4.4''\text{di}(5\text{-nonyl})\text{-}4.4'\text{-bipyridine}$, and for both direct and inverse ATRP, neither sonication nor the presence of hexadecane affected the kinetics and molecular weights. This strongly suggests that this catalyst diffused rapidly through the aqueous phase. Nevertheless, sonication and the presence of hexadecane had a strong effect of particle size. A word of warning was given about the high sensitivity of the Cu(I) to air and the use of homogenization, because if precautions are not taken homogenization may disperse air into the reaction mixture.

Matyjaszewski et al. [199] also produced water-borne statistical and block copolymers using ATRP. Although hexadecane was used in the formulations, no sonication was used, and it is open to discussion whether these reactions could be classified as miniemulsion processes or not.

5.3.4. Reversible addition–fragmentation chain transfer

Moad et al. [200] carried out the CRP of styrene and methyl methacrylate in miniemulsion using 1-phenylethyl dithiobenzoate as RAFT agent. Cetyl alcohol was used as costabilizer and sodium lauryl sulfate as surfactant. Polymerization was stopped at 25% conversion when the PI was 1.18. Stable 20 wt% solids content latexes of controlled MWD (PI = 1.12–1.40) were obtained by de Brouwer et al. [201] using non-ionic surfactants with several monomers (styrene, methyl methacrylate, *n*-butyl acrylate, *i*-butyl acrylate, and ethyl hexyl methacrylate) and RAFT agents. Some increase of PI with conversion, presumably due to bimolecular termination, was observed. Block copolymers were prepared by chain extension. It is claimed that the increased polymerization rate of the compartmentalized system allowed for improved block copolymer purity compared to that of homogeneous systems. Nucleation of particles by processes other than droplet nucleation led to particles containing no RAFT agent and hence to broader molecular weights and mixtures of block copolymers and pure homopolymers.

It is interesting to note that only non-ionic surfactants led to stable latexes whereas both anionic and cationic surfactant produced coagulum and a steadily increasing polydispersity during the reaction. The reasons for this behavior have been investigated by Tsavalas et al. [202]. The presence of large amounts of oligomers was postulated to be the culprit behind the destabilization observed in ionically stabilized miniemulsions. However, no definite proof was offered and no reasons for the stabilization of similar systems with non-ionic surfactants were given. In addition, it is worth noting that oligomers are also produced in SFRP and stable latexes using ionically stabilized miniemulsions have been produced [176,177,184–186] (although rather large amounts of surfactants were used (6–7 wt% vs. about 1.2 wt% in de Brouwer's work). Butté et al. [180] used 1-iodotridecafluorohexane as degenerative chain transfer agent in miniemulsion polymerization, but high polydispersities (PI = 1.47–1.67) were obtained.

Lansalot et al. [203] attempted to perform a CRP using perfluorohexyl iodide ($\text{C}_6\text{F}_{13}\text{I}$) as degenerative transfer agent in conventional emulsion polymerization, but the control of the molecular weight was not possible because $\text{C}_6\text{F}_{13}\text{I}$ did not diffuse to the polymer particles. On the other hand, miniemulsion polymerization using $\text{C}_6\text{F}_{13}\text{I}$ as costabilizer and an anionic surfactant (SLS, 2.5 wt% based on monomer) led to stable 10 wt% solids latexes. An increase of M_n and a decrease of PI during the reaction were observed in batch miniemulsion polymerizations, but PI increased with conversion in semibatch

experiments. It was speculated that possible reasons were that the activation–deactivation reactions involve long chains and these reactions might be diffusionally controlled or chain length dependent.

5.3.5. Stability and nucleation of monomer droplets in CRP

Miniemulsion polymerization has become the main method to produce water-borne well-defined polymers using CRP. However, from the growing body of literature it is evident that stabilization of these latexes during polymerization is more difficult than in the case of regular free radical miniemulsion polymerizations. Thus, large amounts of surfactant should be used to obtain stable latexes in both SFRP [176,177,184–186] and ATRP [197,198] miniemulsion polymerizations. In addition, problems stabilizing RAFT miniemulsions with cationic and anionic surfactants have been reported [201,202]. For the case of RAFT miniemulsion polymerization, Tsavalas et al. [202] suggested that stability problems were related to the fact that for a long period of time, the only polymeric species present in the system are oligomers. Ugelstad et al. [35] showed that oligomers are very efficient swelling agents, and hence they may drastically modify the state of the miniemulsion.

Lou et al. [204] have theoretically analyzed the effect of the oligomers on the swelling of monomer droplets and polymer particles. It was assumed that 1% of the number of monomer droplets became polymer particles, that the monomer conversion in the nucleated droplets was 10%, and that the polymer (oligomer) was equally distributed between these polymer particles. In addition, the length of the oligomers was proportional to monomer conversion and it was assumed that the interfacial tension was 0.025 N/m (about five times greater than the maximum value in systems containing surfactants [4,50]). It was found that under these conditions, and provided that the monomer droplets are small enough ($d_d = 60$ nm in the example presented), the nucleated monomer droplets may become super-swollen increasing their volume by a factor of about 50, namely reaching a particle size of about 220 nm. The effect of the oligomers on swelling becomes negligible when the droplet size was assumed to be 100 nm. Swelling may become extremely high (about 600 times giving particles of 500 nm in diameter) if only a 0.1% of particles is nucleated, and a relatively high conversion (10%) is reached in these particles.

Luo et al. [204] concluded that this superswelling causes the stability problems encountered in CRP in miniemulsion. However, this conclusion is open to discussion. In the first place, the parameters used in the simulations maximize swelling effects. Thus, the interfacial tension used in the calculations (0.025 N/m) was about five times greater than the maximum value in systems stabilized with surfactants (0.005 N/m) [4,50], and Luo et al. [204] showed that swelling becomes negligible if the interfacial tension is 0.020 N/m. The droplet size (60 nm) used in the calculations seems also small for a miniemulsion. Monomer droplets of 100–200 nm are more common [24,47,123] and simulations showed that swelling is negligible for such droplet sizes [204]. Another aspect that is controversial is the view of the nucleation process in CRP miniemulsions implied in the system simulated by Lou et al. [204]. These authors considered that, mimicking miniemulsion polymerization using regular initiators, nucleation in CRP miniemulsions may be slow and hence particles containing a significant amount of polymer coexist with monomer droplets for a long period of time. Such a mechanism would preclude the use of miniemulsion polymerization in CRP, as broad MWDs would be obtained in miniemulsion polymerization because the chains will be initiated at different moments along the reaction. In addition, in the case of ATRP miniemulsion, all droplets contain the catalyst, and considering the high number of chains per particle (a 250 nm particle contains approximately 160 000 chains of $M_n = 30\,000$), it is unlikely that

only a fraction of the droplets undergoes polymerization to a significant extent whereas no polymerization occurs in the rest of particles. Similar arguments may apply to SFRP using alkoxyamines [192].

5.4. Catalytic polymerization

Traditionally, polymerization in aqueous media has been limited to free radical polymerization because water deactivates most non-radical active species (ionic and organometallic). The situation is changing rapidly. In addition to the developments in ATRP and cobaloximines chain transfer agents, highly active water-tolerant catalysts have been discovered. The detailed discussion of these catalysts is out of the scope of this review and the reader is referred to reference [205] for additional details. Here, discussion is restricted to the processes implemented in miniemulsion polymerization: (i) catalytic polymerization of ethylene, and (ii) ring-opening metathesis polymerization.

5.4.1. Catalytic polymerization of ethylene

Tomov et al. [206] produced linear polyethylene terminated in a double bond by means of miniemulsion polymerization using a binuclear nickel-ylide catalyst in the presence of a phosphine scavenger. Productivity was reported to be about 6 kg polymer/g Ni. Large particles ($d_p = 600\text{--}730$ nm) that coagulated to form a ‘cream’ were obtained. No latex was formed when conventional emulsion polymerization was implemented.

Soula et al. [205] developed a nickel(II) keto-ylide catalyst able to polymerize ethylene in water. Coarse dispersions that sedimented rapidly were obtained when a conventional emulsion polymerization was attempted likely due to the fact that the catalyst remained in the big monomer droplets. On the other hand, miniemulsions using hexadecane as costabilizer yielded stable 10% solids latexes. The activity of the catalyst (83 kg polymer/g Ni h) was two orders of magnitude lower than that in organic phase polymerizations, and the activity was not affected by surfactant concentration (the surfactant was not defined). A productivity of 49 kg of a linear polymer per gram of nickel was observed. No correlation between the initial droplet size and the final particle size was observed and the number of polymer particles was always higher than the number of monomer droplets. This result is surprising because this requires the catalyst to diffuse out of the monomer droplets, and considering that the catalyst is very hydrophobic, this is unlikely. Under these circumstances, one wonders about the accuracy of the droplet size determination (carried out by light scattering). Non-spherical particles were obtained. This was attributed to a crystallization rate faster than the particle growth rate.

Recently, Held et al. [207] reported on the polymerization of ethylene in water using both Brookhart catalysts [208] and Klabunde catalyst [209]. However, dispersions consisting of low-molecular weight material with a M_n of 1000 g/mol were obtained. A much higher molecular weight ($M_n = 100\,000$ g/mol) was obtained in miniemulsion polymerization [210].

5.4.2. Ring-opening metathesis polymerization

Claverie et al. [211] used water-soluble ruthenium alkylidene catalysts to polymerize norbornene in emulsion. Less strained olefines such as cyclooctene and 1,5-cyclooctadiene cannot be polymerized with these catalysts but are efficiently polymerized by a commercial Grubbs type catalyst ($\text{RuCl}_2(\text{P-Cy}_3)_2(=\text{CHPh})$). This catalyst is not soluble in water, and hence miniemulsion polymerization with hexadecane as costabilizer and sodium lauryl sulfate as surfactant was implemented. High conversion (typically greater than 90%) was reached in a short process time (5 min). In addition, it was found that

the number of polymer particles was much higher than the number of initial droplets. This result is surprising because the catalyst is very hydrophobic, but no explanation is provided. A completely soluble 1,4-polybutadiene latex was obtained upon miniemulsion polymerization of 1,5-cyclooctadiene.

5.5. Encapsulation of inorganic solids

Encapsulation of inorganic particles in polymer matrices is of interest in cosmetics, pharmaceuticals, paint production and for reinforcing filler particles for polymers [212]. Attempts to encapsulate polymer particles using conventional emulsion polymerization have been reported [213,214] but it was found difficult to locate the dominant polymerization loci at the surface of the inorganic particles. Erdem et al. [212,215,216] showed that the characteristic features of miniemulsion polymerization present advantages as an encapsulation method because the inorganic particles can be directly dispersed in the monomer droplets becoming encapsulated upon polymerization of the miniemulsion droplets. Both a good dispersion of the inorganic particles in the monomer and a stable aqueous miniemulsion of the monomer containing TiO_2 dispersed particles are critical for the success of this method. Erdem et al. [212] investigated the conditions required to obtain a good dispersion of hydrophobic and hydrophilic TiO_2 particles in styrene (or cyclohexane). TiO_2 was dispersed in styrene (or cyclohexane) using ultrasound and several diblock and triblock copolymers as stabilizers. Only polybutene–succinimide pentamine worked well, mostly because of the ability of its amine groups to interact with the hydroxyl groups present on the surface of the TiO_2 . The stability of the hydrophilic TiO_2 (with many –OH groups on the surface) was very good. TiO_2 particle size decreased with the amount of stabilizer and slightly increased with time at 25 °C, although a higher increase was observed at the reaction temperature (70 °C). The hydrophobic TiO_2 was found to be less stable giving bigger particles than the hydrophilic TiO_2 .

Erdem et al. [215] prepared aqueous miniemulsions of the styrene containing TiO_2 dispersed particles by both sonication and a high-pressure homogenizer (Microfluidizer). Sodium lauryl sulfate was used as surfactant and hexadecane plus polystyrene was the costabilizer system. It was found that the presence of TiO_2 particles within the miniemulsion droplets resulted in a significant increase in the droplet size (measured by the soap titration method [66]). Increasing surfactant concentration did not result in a significant change in the size of the miniemulsion droplets. An increase in the loading of the TiO_2 led to larger miniemulsion droplets. It was also found that the use of a more efficient homogenization (high-pressure homogenization vs. sonication) could not significantly reduce the droplet size. Reasons for these results were not provided. The polymerization of these miniemulsions trying to encapsulate the TiO_2 particles was also investigated [216]. It was found that the extent of the encapsulation strongly depended on the quality of the dispersion of the TiO_2 particles in the monomer. The maximum encapsulation efficiencies (83% coverage) were obtained with the smallest TiO_2 particles (hydrophilic particles stabilized with 1.0% of polybutene–succinimide pentamine). Hydrophobic TiO_2 or the use of less stabilizer led to larger TiO_2 particles that resulted in lower encapsulation efficiencies. The failure to achieve 100% encapsulation was attributed to: (i) formation of new particles by homogeneous nucleation; (ii) presence of large TiO_2 aggregates that may not be contained inside the monomer droplets; and (iii) less than 100% nucleation of droplets.

Bechthold et al. [217] coated 120 nm CaCO_3 particles with a layer of stearic acid prior to dispersing 5% of these particles in a mixture of styrene and hexadecane. The resulting dispersion was dispersed in water (20% solids) and polymerized. No free CaCO_3 was observed by TEM, but pure polystyrene particles were detected. The method was also extended to the encapsulation of carbon black. Eight

percent load of carbon black was inhomogeneously incorporated into polystyrene particles. A higher carbon black loading was achieved by Tiarks et al. [218]. These authors dispersed the carbon black in an aqueous surfactant solution by using sonication. A miniemulsion of styrene and a polyurethane costabilizer was prepared using sonication. Then, the miniemulsion was mixed with the aqueous dispersion of carbon black and the resulting dispersion was sonicated. Sonication was repeated once. The resulting dispersion was polymerized with AIBN obtaining stable latexes that contained large fractions of carbon black (40%) with a good coverage of the carbon black. It was found that particle size was not dependent on surfactant concentration, but the process was sensitive to the type and amount of costabilizer used. Hexadecane was less efficient than polyurethane and there is an optimum amount of polyurethane, below which coagulation occurs and above which new particles are formed. The reasons for this behavior remained unclear. Also an optimum monomer/carbon black fraction was found. Larger amounts of monomer yielded pure polymer particles and smaller amounts resulted in uncovered carbon black particles.

5.6. Incorporation of hydrophobic monomers

Polymer films made out of latexes obtained polymerizing hydrophobic monomers present superior water resistance. The incorporation of hydrophobic monomers in the polymer backbone is easier in miniemulsion polymerization as compared with the conventional emulsion process because the need of mass transport through the water phase is minimized by droplet nucleation. Chern et al. [32,43–45] used long chain alkyl methacrylates as both comonomers and costabilizers to prepare styrene/methacrylate copolymer in a batch reactor. Mathauer et al. [219] disclosed a semicontinuous process in which a miniemulsion containing the hydrophobic monomers is fed into the reactor along with a regular preemulsion. It is claimed that this process allows the incorporation of hydrophobic monomers into the copolymer. The miniemulsion homopolymerization of polyorganosiloxane macromonomers having acryloxy or methacryloxy groups has also been reported [220].

Landfester et al. [221] demonstrated the feasibility of polymerization of epoxides with diamines, dithiols and diols in miniemulsion. The epoxides used have a poor water solubility and played the role of the costabilizer. Anionic, non-ionic and polymeric surfactants could stabilize the latex, but large amounts of surfactant were needed (30–40 wt% based on monomer) to obtain stable latexes. Cationic surfactants based on quaternary amine are not favorable because the quaternary amine catalyzes the epoxide ring opening. It was found that increasing the water solubility of either epoxide or amine led to larger particle sizes.

5.7. Hybrid polymer particles

Efforts to develop water-borne coating systems that combine the properties of alkyd resins, epoxy resins and polyurethanes with those of the acrylic latexes are driven by the belief that the positive properties of both polymers can be combined in a synergistic way. It is expected that the properties would improve with an intimate contact between the components of the hybrid latex. This requires a good compatibility between the acrylic polymer and the resin that can be obtained by polymerizing acrylic monomers in the presence of resins containing reactive groups. In addition, a good control of the PSD of the latex is required. This good control of the PSD is difficult to achieve by emulsifying preformed polymers. On the other hand, the use of conventional emulsion polymerization is precluded

because the resins are not soluble in water. Wang et al. [103] attempted to solve this problem by polymerizing miniemulsions formed by sonicating a dispersion of methyl acrylate–PMMA–alkyd resin in water. PMMA played the role of costabilizer. The miniemulsions presented a good shelf stability that increased with the alkyd content. A limiting conversion that decreased with the alkyd content was observed in all polymerizations. It was found that only 20–30% of the double bonds of the alkyd resin reacted. The fraction of the polyacrylate grafted onto the alkyd increased with the alkyd content and ranged from 22 to 70%. The morphology of the resulting hybrid particle was not described. Wu et al. [222] produced hybrid alkyd/acrylic latexes by miniemulsion copolymerization of methyl methacrylate and butyl acrylate in the presence of alkyd resins. The alkyd resin acted as costabilizer but the shelf stability of the miniemulsion was limited (much less than that of the hexadecane stabilized miniemulsions). A minimum amount of alkyd resin (20%) was needed for stabilization. Polymerization rate decreased with the alkyd content because chain transfer to the alkyd produces relatively inactive radicals. Nucleation of particles via micellar or homogeneous nucleation was detected. Only 17–28% of the alkyd double bonds reacted and the GPC trace showed that some alkyd remained ungrafted. The glass transition temperatures of alkyd resin, poly(acrylate-*graft*-alkyd) and poly(acrylate) could be identified by differential scanning calorimetry, although extraction experiments suggested that most of the polymer was poly(acrylate-*graft*-alkyd). The morphology of the hybrid particle was not described.

van Hamersveld et al. [65] attempted producing sunflower oil–acrylate hybrid particles by miniemulsion polymerization. Oil–methyl methacrylate miniemulsions stabilized with sodium lauryl sulfate and hexadecane were prepared by sonication followed by high pressure homogenization. Cryogenic TEM showed that the monomer droplets were homogeneous. Polymerization of the miniemulsions with *t*-butyl hydroperoxide yielded non-homogeneous particles, whereas those initiated with hydroperoxidized sunflower oil/Fe²⁺-ethylenediaminetetracetic acid/sodium formaldehyde sulfoxylate showed no visible phase separation. These results suggest that the oil–acrylate copolymers formed from the hydroperoxidized sunflower oil initiator were able to compatibilize the oil–acrylate hybrid particles. Complete conversion of the MMA was not achieved and it was proposed that at high conversions the hydroperoxidized oil could not diffuse to the particle–water interface, where the redox reaction occurs, and hence not enough radicals were produced.

Gooch et al. [109] also used miniemulsion polymerization to prepare hybrid acrylic/oil-modified poly(urethane), OMPU, latex particles. OMPU is water-insoluble and no additional costabilizer was used to minimize Ostwald ripening. After polymerization, 60–80% of the initial double bonds of the OMPU remained unreacted, and hence available for curing. It was observed that 29–56% of the OMPU was grafted. Surprisingly, grafting efficiency decreased as acrylate monomer/OMPU ratio increased. No explanation was provided and particle morphology was not analyzed.

Tsavalas et al. [140] extended the applications of miniemulsion polymerization to the preparation of hybrid acrylic/polyester water-borne crosslinkable coatings. Miniemulsions of monomers (MMA/BA/AA) and unsaturated polyester resin stabilized with SLS were prepared by sonication. The unsaturated polyester acted as costabilizer. The polymerization rate slightly decreased as the resin content increased. This effect was attributed to chain transfer to the resin that yielded less reactive radicals, although the effect of decreasing monomer concentration as resin content increased may account for a part of the polymerization rate decrease. A limited conversion of 80%, independent of resin content, was observed. Chain transfer to resin was claimed to be responsible for the limiting conversion. About 10% of the double bonds of the unsaturated polyester remained unreacted, and therefore available for curing. Transmission electron micrographs showed separated polyacrylic and polyester phases. It was found

that about 70% of the polymer was crosslinked. The grafted fraction could not be determined by extraction experiments unambiguously, because gel may be formed from the acrylic monomers [223,224]. Latexes showed a good shear and shelf life stability and for solids content lower than 45% resisted two freeze–thaw cycles.

Poly(isobutylene)–poly(diorganosiloxane) latex particles were produced by miniemulsion copolymerization of acrylic or methacrylic functionalized poly(isobutylene) macromonomers with a poly(diorganosiloxane) having acryloxy or methacryloxy groups and with a monomer such as an alkyl acrylate or alkyl methacrylate [225].

The preparation of epoxy resin/acrylic composite particles by miniemulsion polymerization has been recently reported [226]. Epoxy resins have good heat resistance and adhesion, and acrylic polymers have weather and water resistance. These hybrid particles were an attempt to combine these properties. Miniemulsions were formed by using a high shear device, and were stabilized with hexadecane and a mixture of anionic and non-ionic surfactants. It was found that a droplet size smaller than 500 nm was required for stable latexes and a good incorporation of the epoxy resin. Otherwise, many new particles that did not contain epoxy resin were nucleated by homogeneous or micellar nucleation. Functional monomers (methacrylic acid and dimethylaminoethylmethacrylate) were required for good polymerization and storage stability, as well as for film solvent resistance.

5.8. Miniemulsion polymerization in non-aqueous systems

Landfester et al. [141] formulated both direct and inverse polymerizable miniemulsions in non-aqueous media. Direct miniemulsions were exemplified by dispersing styrene in formamide and glycol using hexadecane as costabilizer. It was found that non-ionic surfactants were more effective than ionic surfactants, which was attributed to a low degree of ion solvation and degree of dissociation in formamide. It was possible to make particles as small as 70 nm. Inverse miniemulsions were generated with polar monomers such as hydroxyethyl methacrylate, acrylamide or acrylic acid in cyclohexane or hexadecane as continuous phase. NaCl was used as lipophobe to avoid droplet degradation by diffusion. Particles in the range of 50–200 nm were obtained. Superparamagnetic latexes have been recently produced by inverse miniemulsion polymerization [227].

5.9. Anionic polymerization

Maitre et al. [228] studied the anionic polymerization of phenyl glycidyl ether (PGE) catalyzed by a surface active compound (didodecyldimethyl ammonium hydroxide, $N'OH$) in miniemulsion. Miniemulsions were formed by sonicating a mixture of PGE, $N'OH$, Brij 30 (polyoxyethylene lauryl ether) and water. PGE acted as a weak costabilizer and no additional costabilizer was added. However, PGE is too water-soluble (2×10^{-3} mol/l) and destabilization of the miniemulsion was observed. Nevertheless, increasing the concentration of surfactant led to miniemulsions stable enough to be polymerized. It was found that polymerization rate increased with $N'OH$ concentration and decreased with non-ionic surfactant concentration. The average molecular weights increased with $N'OH$ concentration and by adding pentanol and octanol. In addition, M_n increased along the polymerization. A striking result is that the maximum chain length observed did not exceed eight units whereas longer chain lengths are obtained in bulk polymerization [228]. To account for these results, Maitre et al. [228] proposed that the polymer chains are initiated at the surface of the monomer droplets by the hydroxyl counterions of

N'OH. The resulting alkoxide active centers can then associate with the ammonium group of the N'OH and this ionic pair is stable enough to permit a few propagation steps before chain termination occurs. The dead chains diffuse into the polymer particles without undergoing further propagation reactions. It is postulated that the short oligomers have some affinity for the interface because of their hydroxide end groups, and hence they remain near the surface of the particle increasing the solubility of PGE in this region, which in turn increases polymerization rate and molecular weights. Therefore, the higher the concentration of N'OH, higher is the concentration of short oligomers and higher the polymerization rate and molecular weight. It is believed that the role of the alcohols was also to increase the concentration of PGE in the outer shell of the particle. On the other hand, an increase of the surfactant concentration resulted in a decrease the surface concentration of N'OH leading to lower polymerization rates. According to Maitre et al. [228] the critical chain length was due to the fact that once the chains reached that value, they would lose their surface activity, provoking the disruption of the ion pair and the instantaneous termination.

The same research group [229–231] proposed a similar reaction scheme for the anionic polymerization of octamethylcyclotetrasiloxane (D4) in miniemulsion. In this case, miniemulsion stability was better because D4 is more water-insoluble (2×10^{-7} mol/l) than PGE and can reduce Ostwald ripening. The critical length for termination at the surface of the particles was found to be 30. In addition, condensation and redistribution reactions inside of the polymer particle led to an increase of M_n and a modification of the MWD. Barrère et al. [232] showed that the anionic polymerization of 1,3,5-tris(fluoropropylmethyl)cyclotrisiloxane (F3) in miniemulsion follows a different pattern than in bulk. In both cases, the process occurs in several processes in series. First, linear polymer is formed by propagation, and after monomer reaction, condensation reactions led to higher molecular weight. Finally, backbiting reactions break the polymer chains yielding small cyclic products. It is observed that the extension of backbiting is substantially reduced in miniemulsion polymerization as compared to bulk polymerization. No justification for this result was offered.

5.10. Step polymerization in aqueous dispersed media

Polymers produced by step polymerization have been traditionally produced in bulk and solution polymerizations. Although aqueous dispersions of these polymers do exist (e.g. polyurethane dispersions), they are formed by emulsification of preformed polymer.

Tiarks et al. [142] carried out the one-step preparation of polyurethane aqueous dispersions in miniemulsion. A mixture of diisocyanate, diol, hexadecane, sodium lauryl sulfate and water was homogenized by ultrasonification at low temperature (0 °C) to avoid any reaction. The resulting miniemulsion was polymerized by increasing the temperature to 68 °C. According to the authors, the following requirements should be fulfilled for a successful process: (i) low water solubility of the reactants (not quantified), (ii) the reaction between the diisocyanate and the diol has to be slower than the time needed for the miniemulsion step, and (iii) the reaction of the diisocyanate with water in the dispersed state must be slower than the reaction with the diol. Isophorone diisocyanate and 1,12-dodecanediol or bisphenol A are claimed to fulfill these requirements but the extent of the side reactions was not quantified. In addition, no details about polymer microstructure (composition, MWD) and particle morphology are provided. On the other hand, it was found that hexamethylene diisocyanate was too reactive.

5.11. Production of low-molecular weight polymers in dispersed media

Polymerization in dispersed media typically produces high-molecular weight polymer, however, much lower molecular weights present advantages for certain applications. Catalytic chain transfer using cobaloximes is an efficient way of producing these polymers. In order to be used in conventional emulsion polymerization, the catalytic chain transfer agent should be rather water-soluble to be able to diffuse to the polymer particles through the aqueous phase. However, the catalyst is deactivated by the oxygen-centered peroxide and persulfate radicals produced by the initiators more commonly used in emulsion polymerization [233,234]. These effects can be minimized by separating the catalyst from the source of radicals by using hydrophobic cobaloximes in miniemulsion polymerization [235,236]. Kulkulj et al. [235,236] studied the miniemulsion polymerization of methyl methacrylate costabilized with sodium lauryl sulfate and hexadecane using two cobaloximes of different water solubility: cobaloxime boron fluoride (COBF) that partitions equally between organic and water phases, and tetra phenyl cobaloxime boron fluoride (COPhBF) that resides exclusively in the organic phase. Both water-soluble (KPS) and oil-soluble (AIBN) initiators were used. Using AIBN a strong reduction of M_n was observed using these cobaloximes. The effect of COPhBF was stronger because its concentration in the polymer particles was higher than that of COBF due to the partitioning of COBF. The increase of M_n along the reaction indicated some deactivation of the catalysts. Using KPS, the reduction of M_n with COPhBF was similar to that observed in the case of AIBN, but with COBF M_n was higher than when using AIBN presumably because COBF is deactivated in the aqueous phase by the oxygen-centered sulfate radicals. Particle sizes were not reported.

5.12. Latexes with special particle morphology

Particle morphology affects many application properties including mechanical properties [237]. Latex particles having special morphologies are usually prepared by seeded emulsion polymerization and the final morphology achieved depends on both kinetic and thermodynamic factors [238–242]. Both kinetics and thermodynamics are strongly influenced by polymer–polymer interfacial tensions, and as a rule of thumb the lower the interfacial tension, greater the coverage between phases. Nelliappan et al. [243–244] and Rajatapiti et al. [245–247] attempted to produce well-defined poly(butyl acrylate)–poly(methyl methacrylate) core–shell particles by forming in situ PBA-*graft*-PMMA that could compatibilize the PBA/PMMA composite particles. The PBA-*graft*-PMMA copolymer was formed by copolymerization of BA and a MMA macromonomer. This synthesis could not be carried out in conventional emulsion polymerization because the MMA macromonomer was too hydrophobic and suffered from diffusional limitations. Miniemulsion copolymerization of BA and a MMA macromonomer allowed the production of the seed with a 85% of the reacted MMA macromonomer located at the surface [243]. MMA was polymerized on this seed to form the core–shell latex. It was found that particle morphology strongly depended on the macromonomer concentration. Small amounts yielded hemispherical morphologies, whereas high concentrations resulted in core–shell morphology. The particle approached core–shell morphology as the length of the macromonomer increased [247].

Landfester and Antonietti [248] prepared stable dispersions of poly(acrylonitrile) in the size range of 100–180 nm using miniemulsion polymerization. Due to the insolubility of the polymer in its monomer, such particles are not accessible by classical emulsion polymerization. The particles were composed of 10 nm large polymer nanocrystals. As a consequence, the final latex was not spherical (crumpled

particles). Copolymerization with styrene resulted in a continuous transition between a crumpled and a smooth spherical morphology.

Putlitz et al. [249] prepared ‘armored latexes’ by coating miniemulsion latexes stabilized with cationic surfactants with clay, and using an inorganic polycondensation process to interconnect the clay plates. Although, there is no need for the latexes to be obtained by miniemulsion polymerization, it is claimed that miniemulsions themselves can also be used for encapsulation.

Polymeric nanocapsules were produced by polymerizing a miniemulsion including a monomer and a liquid organic compound in which the polymer was not soluble [250]. Phase separation occurred upon polymerization, and for the adequate choice of monomer, organic compound and surfactant, a core–shell structure in which the core is formed by the organic compound and the shell is formed by the monomer, is the morphology giving the minimum free surface energy. Nanocapsules may be formed by evaporation of the organic compound. Inorganic nanoparticles may be formed by miniemulsifying low-melting point precursor materials [251]. Thus, Fe_2O_3 particles were obtained from molten FeCl_3 droplets by adding a base. Well-defined zirconia particles in an organic phase can also be obtained from a miniemulsion of the low-melting point precursor ZrOCl_2 .

6. Summary

Miniemulsion polymerization combines some useful features of conventional emulsion polymerization (solvent-free, easy thermal control, radical compartmentalization that allows simultaneous high polymerization rate and high molecular weights) with the possibility of using water-insoluble reactants. Droplet nucleation is the distinctive feature of miniemulsion polymerization that allows dealing with hydrophobic reactants because in miniemulsion polymerization the need for mass transfer through the aqueous phase is minimized. In this way, materials that are not accessible by other polymerization techniques can be obtained. Some examples of these polymer materials are: (i) dispersed polymers of well-defined microstructure obtained by CRP; (ii) water-borne linear polyethylene produced by means of catalytic polymerization; (iii) completely soluble 1,4-polybutadiene latexes obtained by ring-opening miniemulsion polymerization; (iv) hydrophobic latexes obtained from hydrophobic monomers; (v) encapsulated inorganic particles; (vi) hybrid water-borne coatings; (vii) superparamagnetic latexes; and (viii) low-molecular weight latexes. In addition, droplet nucleation allows cycling-free operations in backmixed continuous reactors and the production of high solids low viscosity latexes. These are merely examples of polymer materials prepared by miniemulsion polymerization, and most likely many others will be developed in the near future. Admittedly, some of these processes are not ready for commercial implementation because the latexes were synthesized under conditions (e.g. very low solids contents, batch process) that are not viable in industrial practice. Efforts should be devoted to investigate miniemulsion polymerization under industrial-like conditions (high solids and semicontinuous processes).

On the other hand, the fundamental knowledge about the processes involved in the preparation and polymerization of monomer miniemulsions is still limited. The effect of the homogenization conditions and the surfactant–costabilizer system on the DSD is not fully understood. The mechanisms involved in droplet nucleation, which is the key aspect of the process, are not known, the lack of a reliable method for the determination of the DSD being the bottleneck of this research. Future research should address this point. Other aspects that will require attention are particle morphology and the development of

predictive mathematical models. These efforts will accelerate the commercial implementation of mini-emulsion polymerization.

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