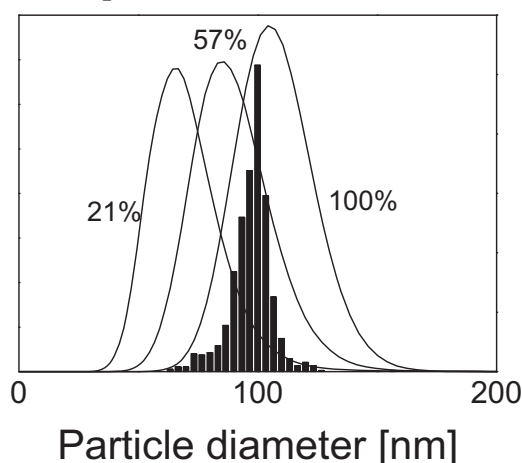


On the Reaction Characteristics of Miniemulsion Polymerization with Aqueous Phase Initiation – Experiments and Modeling

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Miniemulsions, consisting of submicron droplets of very hydrophobic lauryl methacrylate or 4-*tert*-butyl styrene, are successfully polymerized using water-soluble sodium persulfate. Monitoring the calorimetric profile as well as the droplet and particle size distribution with conversion manifests a process of monomer redistribution, droplet disappearance, and narrowing of the particle size distribution. The observed reaction characteristics could be modeled adequately, using thermodynamic principles. The results of the work presented do not only have predicting value, but also enfeeble the idea of a one-to-one translation of monomer droplets into polymer particles in miniemulsion polymerization.



1. Introduction

Miniemulsion polymerization is a heterogeneous polymerization technique in which radical entry takes place in monomer droplets rather than in monomer-swollen micelles.^[1–3] Monomer droplets, usually in the order of 50–500 nm, are created by the application of high shear, via e.g., ultrasonication,^[4] high shear homogenization,^[5] or more recently, static mixing.^[5,6] This additional step, reducing its attractiveness for commercial use, is counter-

balanced by the claimed advantages of miniemulsion polymerization, such as the use of very hydrophobic monomers^[7,8] or the ability to obtain higher solid contents.^[9,10] A property, often ascribed to miniemulsion polymerization, is the so-called one-to-one copy of monomer droplets into polymer particles. This means that droplets do not change size, size distribution, or composition upon polymerization. Therefore, each monomer droplet would act as an individual nanoreactor, i.e., a segregated system. The validity of this feature is, however, highly disputable. Landfester et al.^[11] claim, by using small-angle neutron scattering, to have proven that there is no difference between droplets and particles in the miniemulsion polymerization of styrene (STY). Cheng et al.^[12] conclude, based on dynamic light scattering measurements (DLS) that droplet identity preservation was achieved in STY miniemulsions. Nevertheless, the idea that an exact copy is an exception rather than a common feature is much more widespread. Miller et al.^[13,14] demonstrated that the average particle diameter in a miniemulsion polymerization depends on the initiator concentration and increases

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with increasing conversion. This observation has been made by Choi et al.^[15] too, who also showed that a hydrophobic initiator (2,2'-azobis-(2-methyl butyronitrile) or AMBN) gave broader particle size distributions (PSD) than hydrophilic potassium persulfate. Lin et al.^[16] showed that the polydispersity of the particle size distribution narrows with increasing conversion. Yildiz et al.^[17] have shown that the correspondence between droplets and particles in a lauryl methacrylate (LMA) miniemulsion polymerization is much better with AIBN (azobis-isobutyronitrile) initiation than with potassium persulfate initiation. In the latter case, an increase in particle number was observed, which was attributed to droplet budding, i.e., the splitting of nucleated particles throughout polymerization. Mixtures of separately prepared miniemulsion droplets, each consisting of only one monomer, showed a copolymer after polymerization rather than two separate homopolymers.^[18,19] Ugelstad et al.^[20] derived a theoretical relationship between the particle diameter and the volumetric growth rate for seeded emulsion systems, thereby showing that concentration differences between differently sized particles can occur during polymerization, possibly resulting in monomer redistribution.

1.1. Thermodynamics

Miniemulsions are kinetically, but not thermodynamically, stable. Monomer droplets will strive towards minimal interfacial energy. Degradation can take place either via coalescence of droplets, thereby reducing the number of droplets, or Ostwald ripening, the diffusion of monomer from small to large droplets, which will affect the polydispersity of the distribution. Coalescence can be minimized by adjusting the surfactant type and concentration, whereas the effects of Ostwald ripening can be reduced by including a so-called costabilizer in the formulation, a low molecular weight highly water-insoluble component such as hexadecane (HD). The low water solubility is thought to prevent the costabilizer from migrating between monomer droplets. As a result, Ostwald ripening will result in an osmotic pressure difference between differently sized droplets, thereby creating a driving force for monomer transport in the opposite direction, thus maintaining droplet size distribution. Droplet thermodynamics is commonly described using the difference in monomer molar differential Gibbs-free energy ($\overline{\Delta G_m}$) between the monomer in a monomer droplet and in its reference state, in our case a free monomer phase. This difference is given by the Morton equation:^[21]

$$\begin{aligned} \frac{\overline{\Delta G_m}}{RT} = & \ln(\phi_m) + (1 - m_{mh}) \cdot \phi_h \\ & + \chi_{mh} \cdot \phi_h^2 + \frac{4 \cdot \gamma \cdot \overline{V_m}}{RT \cdot d_d} \end{aligned} \quad (1)$$

In Equation (1), ϕ_m and ϕ_h represent the volume fractions of monomer and hydrophobe, m_{mh} the ratio of molar volume between monomer and hydrophobe, χ_{mh} the Flory–Huggins interaction coefficient between monomer and hydrophobe, $\overline{V_m}$ the monomer molar volume, γ the droplet–water interfacial tension and d_d the droplet diameter. It is assumed that the droplet only consists of monomer and hydrophobe. Monomer will strive toward zero chemical potential difference between various droplets by monomer redistribution. When no transport of hydrophobe is assumed, this monomer redistribution can be determined analytically as function of droplet diameter and hydrophobe concentration for two droplets by equating their chemical potential functions.^[1] When a droplet also contains polymer, Equation (1) has to be extended to:^[22,23]

$$\begin{aligned} \frac{\overline{\Delta G_m}}{RT} = & \ln(\phi_m) + (1 - m_{mh}) \cdot \phi_h + \phi_p + \chi_{mh} \cdot \phi_h^2 \\ & + \chi_{mp} \cdot \phi_p^2 + \phi_h \cdot \phi_p \cdot (\chi_{mh} + \chi_{mp} - \chi_{hp} \cdot m_{mh}) \\ & + \frac{4 \cdot \gamma \cdot \overline{V_m}}{RT \cdot d_d} \end{aligned} \quad (2)$$

with ϕ_p the volume fraction of the polymer and χ_{mp} and χ_{hp} the Flory–Huggins interaction parameters between the monomer and the polymer and between the hydrophobe and the polymer, respectively. Many authors take into account that droplet diameters change upon Ostwald ripening.^[24–27] However, very few authors pay attention to the thermodynamic implications of disappearance of monomer and the formation of polymer during a miniemulsion polymerization. Delgado et al.^[28,29] provided a thorough review on the effect of thermodynamics in a miniemulsion (co)polymerization. By incorporating thermodynamics in their mathematical model, they were able to predict the mass transfer between individual particles throughout an emulsion copolymerization. However, they did not take into account the effect on the particle size distribution. Rodriguez et al.^[30,31] used droplet thermodynamics to estimate the equilibrium concentration in simulating mass transfer with and without polymerization. Equation (2) implies that the monomer chemical potential in a monomer droplet or partially polymerized particle is depending on the polymer fraction and therefore on conversion, as will be shown later in Figure 4. If monomer would be compartmentalized in these droplets and no monomer redistribution would take place, a chemical potential difference between various particles would arise. In conventional emulsion polymerization, however, the free monomer droplets maintain zero chemical potential difference between the various growing polymer particles by supplying monomer. The large diameter of these droplets (typically 1–10 μm) allows for a negligible surface interaction term, giving it zero chemical

potential difference with its reference state. Consequently, the monomer that is inside the growing polymer particles, that is in chemical equilibrium with the free monomer droplets, also has zero chemical potential difference. Maintaining chemical equilibrium in miniemulsion polymerization, therefore, has to come from monomer rearrangement between nucleated and non-nucleated droplets, thereby influencing the particle size distribution. In this chapter, the reaction characteristics and the evolution of the particle size distribution of a batch miniemulsion polymerization using aqueous phase initiation is determined experimentally. By using thermodynamic principles, we were able to simulate and understand the observed behavior.

2. Experimental Section

2.1. Materials

Styrene (STY; >99%), 4-*tert*-butyl styrene (TBS; 93%), LMA (96%), octadecyl acrylate (ODA; 97%), and HD (99%), were obtained from (Sigma–Aldrich). Sodium persulfate (SPS) was obtained from BASF. Sodium carbonate (SC; >99%) and sodium dodecyl sulfate (SDS; >99%) were obtained from Merck. Inhibitor removal was done by passing the monomers over a column containing inhibitor remover (Sigma–Aldrich) or by distillation under reduced pressure in the case of STY. ODA was used as received. All other chemicals were used as received. In all experiments, deionized water (MilliQ standards) has been used.

2.2. Procedure

Miniemulsions were prepared according to the formulation in Table 1. Hexadecane was dissolved in the monomer. SC and SDS were dissolved in water in a separate beaker. A small aliquot of the water (10–20 g) was kept aside, in which the SPS was dissolved. The monomer and the aqueous phase were mixed together in a beaker, stirred for 10 min and placed in an ice bath. Subsequently, the mixture was sonified for 30 min (45 min in case of the calorimetric measurements) using a Branson CV33 horn powered by a Sonics Vibracell VCX 750W at 65% output.

Calorimetric measurements have been performed using a Mettler-Toledo RC1e HP60 reaction calorimeter (reactor volume 1.6 dm³). This calorimeter is equipped with a pitch blade impeller (six blades, pitch angle 45°, 250 rpm), a calibration heater, and a temperature sensor. The RC1e was operated in isothermal mode using IControl 5.0 software. The miniemulsion was transferred to the reactor and purged for at least 30 min with argon at room temperature using a tube immersed in the miniemulsion. The reactor was then closed and brought to an argon pressure of 2.8 bar absolute. Subsequently, the reaction mixture was calibrated for 30 min at 5 W calibration power. Calibration took place at room temperature instead of reaction temperature to minimize degradation of the miniemulsion. After calibration, the reactor contents were brought to reaction temperature (60.0 ± 0.1) °C and the reaction was started by mechanically adding the initiator, dissolved in 20 ml water and purged with argon. After polymerization, the resulting latex was brought to room temperature and calibrated again. Conversion was measured via residual monomer determination by gas chromatography (GC), after ultrasonication, calibration, and reaction using a GC flame ionization detector (FID) set-up consisting of a Shimadzu GC-2010, equipped with an a-polar column (Varian Chrompack Capillary GC Column CP-SIL 5CB 25 × 0.25 × 0.25 μm) with a packing/coating that consists of 100% dimethyl polysiloxane. Helium was used as carrier gas and an oven temperature gradient from 50 to 300 °C in 5 min was applied. Conversion was measured against both an internal (HD) and external (toluene) standard. The calorimetric conversion–time history was scaled to the measured final conversion.

Glass reactor experiments have been performed using a 400 ml round bottom reactor, equipped with a reflux condenser and a four bladed impeller. The miniemulsion was charged into the reactor and purged for 30 min at room temperature. Subsequently, the reactor was brought to reaction temperature by immersing it in a thermostated water bath at (60.0 ± 0.2) °C. Polymerizations were started by injecting the argon-purged initiator solution. Samples (1–2 ml) were taken throughout the reaction. Polymerization in these samples was short stopped by adding a few mg hydroquinone. Conversion was measured on a Perkin-Elmer Clarus 500 gas chromatograph, equipped with an Agilent Technologies HP-FFAP column. Nitrogen was used as carrier gas with an oven temperature gradient from 50 to 300 °C in 5 min. The conversion was measured against both an internal (HD) and external (toluene) standard.

Table 1. Standard miniemulsion formulations.

Component	Mass [g]	Mass calorimetric experiments [g]	Concentration [mol dm ⁻³] _{aq}
Water	190	780	–
Monomer	50	200	–
Hexadecane	2	8	–
Sodium dodecyl sulfate	1	4	0.017
Sodium persulfate	0.476	1.905	0.010
Sodium carbonate	0.212	0.848	0.010
Water for initiator	10	20	–

2.3. Particle Size Analysis

(cryo-)Transmission electron microscope (TEM) images were made using a FEI Tecnai 20 (type Sphera) TEM, operated with a 200 kV LaB6 filament and a bottom mounted 1024 × 1024 Gatan CCD camera. Pictures were taken at a magnification of 7 800. PSD were determined using ImageJ software.^[32] Images were binarized using a luminance threshold. Subsequently, particles were digitally distinguished from the noise, and the particle area was determined. The particle volume average diameter (d_v), the number average diameter (d_n), and the polydispersity (PDI) were calculated according to:

$$d_v = \frac{\sum (n_i \cdot d_i^4)}{\sum (n_i \cdot d_i^3)} \quad (3)$$

$$d_n = \frac{\sum (n_i \cdot d_i)}{\sum (n_i)} \quad (4)$$

$$\text{PDI} = \frac{d_v}{d_n} \quad (5)$$

in which d_i is the particle diameter of a certain size i and n_i is the number of particles of size i . The number of particles per unit volume of water in a latex (N_p) is calculated via the average particle diameter:

$$d_{\text{avg}} = \sqrt[3]{\frac{\sum (n_i \cdot d_i^3)}{\sum (n_i)}} \quad (6)$$

$$N_p = \frac{6 \cdot V_{\text{mon}} \cdot \rho_{\text{mon}}}{\pi \cdot d_{\text{avg}}^3 \cdot V_{\text{aq}} \cdot \rho_{\text{pol}}} \quad (7)$$

where V_{mon} and V_{aq} are the monomer and aqueous phase volumes, and ρ_{mon} and ρ_{pol} denote the densities of monomer and polymer. Intensity average (z_{avg}) droplet and particle diameters for the calorimetric measurements have been determined via DLS using a Malvern Zetasizer Nano. Miniemulsions and final latex products were diluted in deionized water, containing 3.3 g dm⁻³ SDS at (20.0 ± 0.1) °C. When STY miniemulsions were measured, this surfactant solution was saturated with STY. The Zetasizer has an internal filter which is automatically adjusted to give a count rate of ≈250 kcounts s⁻¹. Reported values are averaged over three runs comprising 16 measurements of 20 s each. Intensity average droplet and particle diameters for the glass reactor experiments have been determined by DLS using a Brookhaven Instruments BI-9000AT correlator with a Brookhaven BI-200SM goniometer set to a scattering angle of 90° and a 17 mW HeNe laser (632.8 nm wavelength). Samples were diluted with 3.3 g dm⁻³ SDS solution to give a count rate of ≈150 kcounts s⁻¹ at the detector and, after temperature equilibration, were subjected to 10 successive analyses of 1 min each. The temperature of the jacket fluid was held at (25 ± 0.1) °C and the exact jacket temperature was used as input when the data was analyzed using Brookhaven Particle Sizing Software v3.72 to obtain individual values of the particle diameter

for each of the ten measurements, the average of which was used to obtain the reported value (the standard deviation of which was typically ≈2 nm). Blank measurements indicated that SDS micelles had no detectable influence on the results. For all DLS measurements, the width of the distribution is indicated by the so-called poly, which is defined as twice the dimensionless ratio of the first two coefficients of the polynomial used to fit the logarithm of the correlation function in the cumulants analysis.

Particle size distributions of the latex products of the glass reactor experiments were also determined using a Polymer Laboratories Particle Size Distribution Analyzer (PSDA). Samples were diluted in a commercially available PSDA eluent (Agilent Technologies). The column was calibrated at regular intervals, using ThermoScientific Duke polystyrene standards in the range of 50–1 000 nm.

The modeling work was performed using Matlab R2012b (64 bit version) using the optimization toolbox.

3. Results and Discussion

3.1. Experimental Results

Figure 1 shows the calorimetric data for the miniemulsion polymerization of STY, TBS and LMA. These monomers were selected based on their water solubilities, which span orders of magnitude from STY (3 × 10⁻² mol dm⁻³ at 25 °C),^[33] via TBS (≈10⁻⁵ mol dm⁻³ at 25 °C)^[8] to LMA (5 × 10⁻⁸ mol dm⁻³).^[34] Complete conversion is obtained within 2 h. It is apparent from the conversion–time histories (Figure 1a) that polymerization starts almost immediately after addition of the initiator. The inhibition effects that are attributed to the miniemulsion polymerization of very hydrophobic monomers have not been observed by us.^[35] When looking at the rates of polymerization (Figure 1b), a few things are noteworthy. The characteristic peak observed at very low conversion is an artifact of the RC1e reaction calorimeter, induced by a heat supply to compensate the addition of a cold water/initiator feed. Furthermore, a clearly visible “plateau” (TBS and LMA) or even increase (STY) in the rate of polymerization can be observed, comparable to conventional emulsion polymerization. The rate of polymerization is given by Equation (8):

$$r_p = \frac{k_p \cdot [M]_p \cdot \bar{n} \cdot N_p}{N_{\text{Av}}} \quad (8)$$

with r_p being the rate of polymerization (mol · dm⁻³ · s⁻¹), k_p , the propagation rate coefficient, $[M]_p$, the monomer concentration in the monomer droplets or polymer particles, $\bar{n}$, the average number of radicals per particle, N_p , the particle number per volume of water and N_{Av} , Avogadro's number. When monomer is compartmentalized in the particles, a gradual decrease in monomer concentration and, therefore, rate of polymerization would have been observed. However, when nucleation of droplets

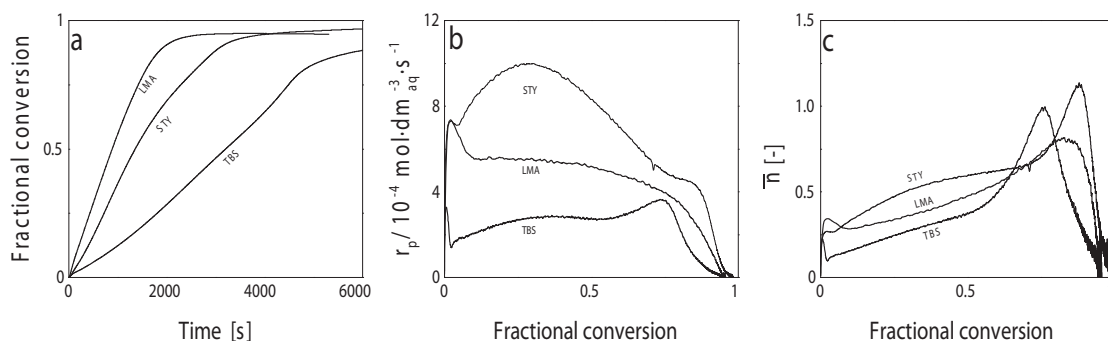


Figure 1. Calorimetric data for three miniemulsion polymerizations using styrene (STY), 4-*tert*-butyl styrene (TBS), and lauryl methacrylate (LMA) as monomer, displaying (a) conversion–time histories, (b) rates of polymerization and (c) average number of radicals per particle (based on final particle number).

continues relatively long after the addition of initiator, the number of the loci of polymerization will increase, counteracting the former effect. Finally, when droplets are not nucleated at all, they will supply their monomer to the nucleated particles, resulting in a constant monomer concentration inside these particles. Using Equation (8), it is possible to derive an overall value for $\bar{n}$, the average number of radicals per particle (Figure 1c). For this, the monomer concentration inside the polymer particles is assumed to decrease linearly with conversion. The IUPAC values for k_p at 60 °C have been used for STY ($341 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) and LMA ($1\,280 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$).^[36] To the best of our knowledge, no measured k_p is available for TBS, and for that, we used the value of STY as suggested before.^[37] Particle numbers were calculated using the average diameter (d_{avg}) of the final latex as determined by (cryo-)TEM, and were assumed to be constant throughout the polymerization. The monomer concentration in the polymer particles is assumed to decrease linearly with conversion. For each miniemulsion polymerization, values close to 0.5 have been calculated for conversions up to 70%, where a gel effect starts. The increase of $\bar{n}$ with conversion gives a strong indication that the number of particles is not constant throughout polymerization, resulting in the presence of monomer droplets even up to high conversion. Measured particle diameters for these reactions can be found in Table 2. PSD are presented in Figure 2.

The use of hydrophobic monomers in combination with DLS is very advantageous, since dilution of the original miniemulsion results in negligible dissolution of the monomer. Final latex products display very narrow PSDs, both visible from TEM analysis as well as from DLS measurements. The difference in poly values between the droplets and particles indicates that the droplet size distribution in the miniemulsion is significantly broader than the final PSD. As a consequence, the measured z_{avg} particle and droplet diameter are not in agreement. The dependency of this parameter on the 4th power of the particle and droplet diameter results in a dominant contribution of big droplets over small droplets.

To obtain an impression of the development of the particle diameter with conversion, the PSD was followed using both DLS and PSDA analysis. The PSDA is the particle size equivalent of size exclusion chromatography (SEC), in which particle diameters are separated based on their size using a packed column with porous beads. Since this technique does not give reliable results for the determination of monomer droplet sizes, due to droplet deformation, only polymer particles (i.e., droplets with a certain polymer volume fraction) can be determined using the PSDA. DLS and PSDA are therefore complementary, since DLS does not distinguish between droplets and particles. Figure 3 shows the combined DLS and PSDA results for three LMA miniemulsion polymerizations, using the formulation from Table 1 but with 0.5, 1, and 2 times the amount of initiator.

Table 2. Average (d_{avg}), volume average (d_v), and number average (d_n) particle diameters and polydispersities obtained from final latex products of styrene (STY), 4-*tert*-butyl styrene (TBS) and lauryl methacrylate (LMA), created by miniemulsion polymerization, as well as z_{avg} particle and droplet diameters and poly values.

	d_v [nm]	d_n [nm]	d_{avg} [nm]	PDI [–]	z_{avg} droplets [nm]	Poly [–]	z_{avg} particles [nm]	Poly [–]
STY	94	91	92	1.03	128	0.132	92	0.017
TBS	104	102	103	1.02	149	0.136	109	0.028
LMA	121	110	113	1.10	176	0.111	127	0.014

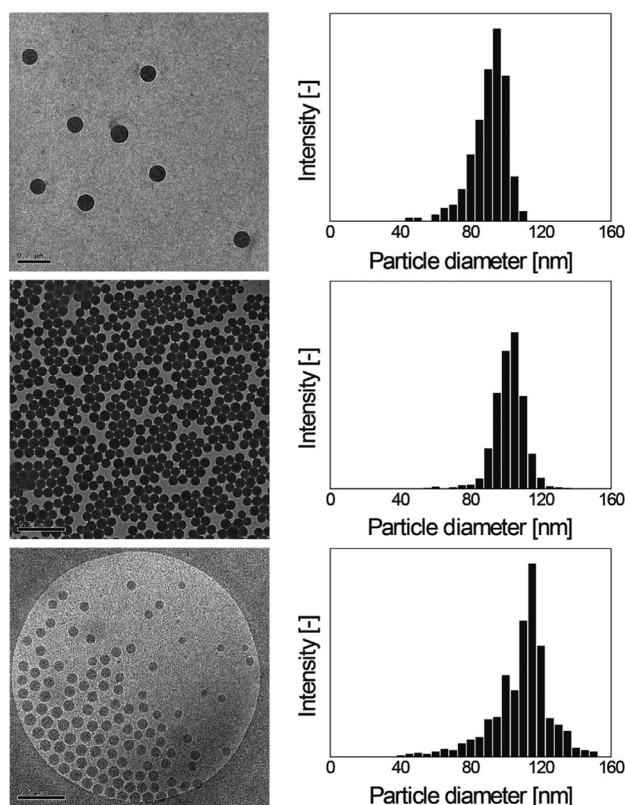


Figure 2. (Cryo-)transmission electron microscopy images and derived particle size distributions for miniemulsion polymerizations of styrene (top), 4-*tert*-butyl styrene (center) and lauryl methacrylate (bottom). Number of particles counted: 248 (styrene), 1134 (4-*tert*-butyl styrene), 681 (lauryl methacrylate).

The DLS experiments (Figure 3a) show a gradual decrease in z_{avg} diameter with conversion up to approximately 40% overall conversion, after which no measurable difference in particle diameter is detected anymore. These observations are in line with similar experiments carried out on STY miniemulsions, using hydrophobic monomers^[38,39] or low molecular weight polymer^[16] as costabilizer. The transition point at which the measured z_{avg} diameter levels off in these reports is determined to be 36 and 40%, respectively. In these studies, the decrease in particle size (and consequently the increase in particle number) was attributed to homogeneous nucleation, a nucleation mechanism rather unlikely for LMA at low stirring speeds.^[8] However, the broadness of the distribution gives more clarity. As can be seen from Figure 3a, the polydispersity of the miniemulsion/latex is also decreasing with increasing conversion. The point at which the poly value levels off cannot be determined very accurately, but it seems to be around 40–50% overall conversion. At low conversion, the polydispersity seems to increase, however,

which will be discussed later. Since the z_{avg} is an intensity average diameter, its value is dependent on the particle diameter to the 6th power. The decrease in measured diameter is, therefore, at least to some extent caused by the redistribution of monomer from large particles and droplets to smaller ones. It is important to recall, at this point, that the DLS measures a mixture of particles and droplets. To differentiate between droplets and particles, the PSD at different conversion was determined for all three LMA miniemulsion polymerizations (Figure 3b–d) using PSDA technology. The final PSD was also determined by cryo-TEM. It is clear that the final volume average particle size depends on the initiator concentration. The PDI values, however, are similar for all polymerizations, being 1.04–1.07 (TEM) or 1.07 (PSDA). Although this dependency of the average particle diameter on the initiator concentration has been observed previously,^[13] it cannot be attributed to an initiator concentration effect solely, as these polymerizations suffered from long inhibition periods after addition of the initiator (10–50 min, inversely related to the initiator concentration). As such, at least part of this phenomenon might be caused by droplet disappearance due to coalescence. The absence of monomer peaks in the PSDA chromatogram indicates that the measured distribution is a distribution of swollen particle diameters, i.e., particles containing both monomer and polymer. Particles grow throughout the polymerization, indicating that there should be a source of monomer, which can be either non-nucleated droplets or large particles giving up monomer to smaller ones. Miller et al.^[13] demonstrated that droplets exist up to 60% conversion, an observation that is supported by the end of the so-called plateau in the rate of polymerization (Figure 1b).

3.2. Model Development

It is clear, based on the aforementioned results that monomer rearrangement is taking place in these miniemulsion polymerizations using SPS, resulting in latex products with a narrow PSD. The driving force for this transport is a difference in the monomer chemical potential for the monomer present in the various individual particles or droplets. For a 100 nm particle in an infinite volume, the decrease in chemical potential with the polymer volume fraction, according to Equation (2), is given in Figure 4.

Monomer data of LMA has been used in this calculation. The ratio of molar volumes for LMA and HD results in an m_{mh} of 1.00. Flory–Huggins interaction parameters have been calculated at 60 °C using the procedure reported by Van Krevelen and Te Nijenhuis,^[40] giving $\chi_{mh} = 0.38$, $\chi_{hp} = 0.37$, and $\chi_{mp} = 0.34$. For the interfacial tension, an estimated value of $5 \times 10^{-3} \text{ N m}^{-1}$ has been used while a possible influence of the composition on the surface tension has not been taken into account.^[1,31] The presence of

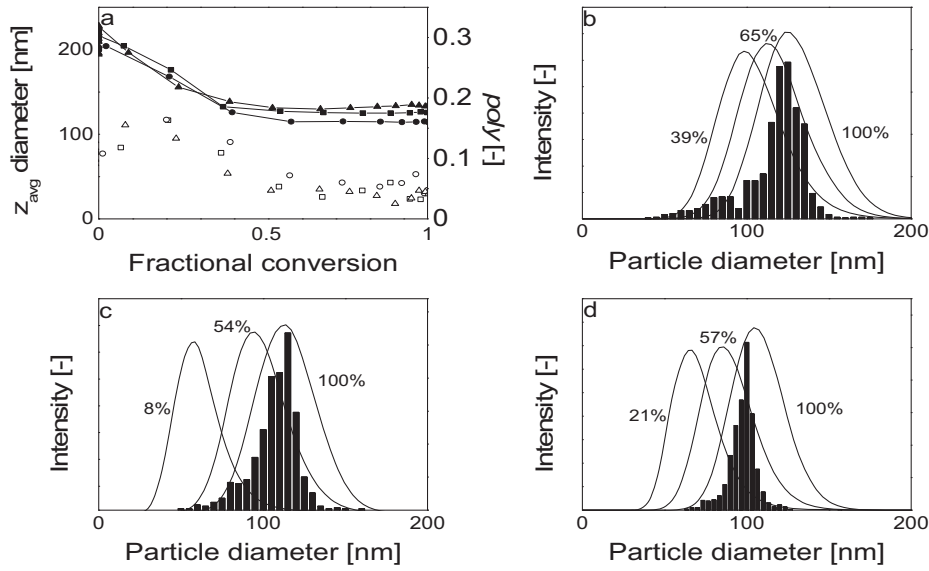


Figure 3. Particle size analysis for lauryl methacrylate miniemulsion polymerizations with varying initiator concentration: (a) z_{avg} diameter (closed symbols) and poly values (open symbols) obtained via dynamic light scattering for ($\blacktriangle$) 0.5 ($\blacksquare$) 1.0, and ($\bullet$) 2.0 times the standard initiator concentration, (b–d) particle size distributions at various conversions via PSDA (curved lines) and final conversion via transmission electron microscopy (histogram) for 0.5 (b, 1 074 particles), 1.0 (c, 648 particles), and 2.0 (d, 1027 particles) times the standard initiator concentration.

hexadecane (4 vol%) was taken into account. At these high costabilizer concentration, the contribution of the surface energy to the total chemical potential is outweighed by the entropic and enthalpic contributions, justifying the assumption on the interfacial tension. Thus, the origin of the difference in chemical potential between particles is caused by a difference in monomer volume fraction. A mini-emulsion polymerization in which the polymerization rate in each particle is linear with the particle volume (“pseudo-bulk kinetics”) would result in a latex with a final PSD very close to the original droplet size distribution, given that every droplet becomes a particle. Note that this does not

mean that no monomer transfer takes place: compositional differences can still result in a chemical potential difference, leading to monomer transfer. On the other hand, when the rate of polymerization (mol s^{-1}) is the same in every particle (“zero-one kinetics”), the chemical potential would decrease much faster in small particles than in large particles. Consequently, redistribution of monomer would result in a net monomer transfer from large particles to small particles, decreasing the PSD and the volume average diameter. This behavior was to some extent predicted by Ugelstad et al.,^[20] based on radical adsorption and desorption kinetics in seeded emulsion polymerization, and qualitatively described by Hansen and Ugelstad.^[41] Monomer droplets that have not been nucleated will not alter their chemical potential, and as a result, will give up monomer to nucleated particles regardless their sizes. We can model this monomer transfer and decrease of the PSD for a set of (randomly sized) N monomer droplets. Each monomer droplet contains an initial amount of monomer, hexadecane and polymer, based on the chosen formulation. The amount of monomer P_{mon} (mol) that is converted inside particle i during a certain time Δt is given by:

$$P_{\text{mon}, t+\Delta t}^i - P_{\text{mon}, t}^i = \frac{-k_p \cdot [M]_d \cdot n \cdot \Delta t}{N_{\text{Av}}} \quad (9)$$

This expression differs from Equation (8) by the use of the actual number of radicals in a particle (n) rather than the average number ($\bar{n}$). The time interval does not

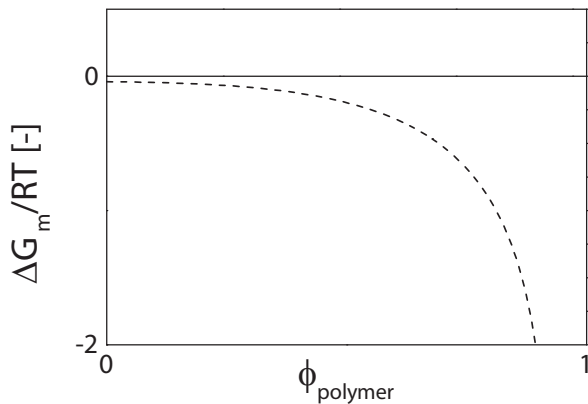


Figure 4. Calculated monomer chemical potential difference as function of polymer volume fraction. $T = 60^\circ\text{C}$, $\phi_h = 0.04$.

necessarily have to be infinitesimally short as is usual the case in numerical approximations, since it resembles the time between consecutive radical entries (usually 1–10 s). Consequently, for every particle the amount and volume of monomer (V_{mon}^i) and polymer (V_{pol}^i) and the particle volume (V_{particle}^i) can be calculated by:

$$V_{\text{mon}, t+\Delta t}^i = \frac{P_{\text{mon}, t+\Delta t}^i \cdot M_{w, \text{mon}}}{\rho_{\text{mon}}} \quad (10)$$

$$m_{\text{pol}, t+\Delta t}^i = m_{\text{pol}, t}^i + (Q_{\text{mon}, t+\Delta t}^i - Q_t^i) \cdot M_{w, \text{mon}} \quad (11)$$

$$V_{\text{pol}, t+\Delta t}^i = \frac{m_{\text{pol}, t+\Delta t}^i}{\rho_{\text{pol}}} \quad (12)$$

$$V_{\text{particle}, t+\Delta t}^i = V_{\text{pol}, t+\Delta t}^i + V_{\text{mon}, t+\Delta t}^i + V_{\text{HD}, t+\Delta t}^i \quad (13)$$

in which $Q_{\text{mon}, t}^i$ is the molar quantity of monomer in particle i at time t , V_x^i , the volume of component x in particle i , m_{pol}^i the mass of polymer in particle i , $M_{w, \text{mon}}$ the monomer molar mass and ρ_{pol} and ρ_{mon} the polymer and monomer density. All substances were assumed to mix isometrically. The monomer volume fraction (ϕ_{m}^i) is then easily obtained by:

$$\phi_{\text{m}, t+\Delta t}^i = \frac{V_{\text{mon}, t+\Delta t}^i}{V_{\text{particle}, t+\Delta t}^i} \quad (14)$$

For hexadecane and polymer, the volume fractions can be calculated analogously. With these volume fractions, the chemical potential of the monomer in every droplet can be calculated using Equation (2). To restore chemical equilibrium in the system, the monomer chemical potentials in all the droplets have to be equalized, which can be done by:

$$\Delta G_{\text{m}}^i - \Delta G_{\text{m}}^{i-1} = 0 \quad i = 2 \dots N \quad (15)$$

By assuming that polymer and hexadecane are compartmentalized in the droplets, equilibration has to come from monomer rearrangement. Assuming that the time constant for interparticle monomer transport is much smaller than the time constant for polymerization, Equation (15) is solved numerically by setting a restriction for the residual sum for the monomer concentration:

$$\sum_{i=1}^n (V_{\text{mon}, t+\Delta t}^i - V_{\text{mon}, t+\Delta t, \text{rearr}}^i) = 0 \quad (16)$$

where $V_{\text{mon}, t+\Delta t, \text{rearr}}^i$ is the monomer volume in particle i after rearrangement. Please note that, when no polymerization takes place, the model simply describes the Ostwald ripening process for a set of N particles.

The actual number of radicals was derived from the approximation for $\bar{n}$, as proposed by Nomura and Fujita:^[42,43]

$$\bar{n} = \frac{1}{2} \times \left(\left[\left(\alpha'_{\text{w}} + \frac{\alpha'_{\text{w}}}{m} \right)^2 + 2 \cdot \left(\alpha'_{\text{w}} + \frac{\alpha'_{\text{w}}}{m} \right) \right]^{1/2} - \left(\alpha'_{\text{w}} + \frac{\alpha'_{\text{w}}}{m} \right) \right) + \left(\frac{1}{4} + \frac{\alpha'_{\text{w}}}{2} \right)^{1/2} - \frac{1}{2} \quad (17)$$

Aqueous phase termination is assumed to have a negligible effect on the radical population. The parameter α'_{w} is the ratio of radical production and radical termination, m is the ratio between radical desorption and termination:

$$\alpha'_{\text{w}} = \frac{2 \cdot f \cdot k_{\text{d}} \cdot [\text{I}_0]_{\text{aq}} \cdot N_{\text{Av}} \cdot \pi \cdot d_{\text{d}}^3}{6 \cdot k_{\text{tp}} \cdot N_{\text{p}}} \quad (18)$$

$$m = \frac{k_{\text{des}} \cdot N_{\text{A}} \cdot \pi \cdot d_{\text{d}}^3}{6 \cdot k_{\text{tp}}} \quad (19)$$

with f the initiator efficiency, k_{d} the initiator (thermal) decomposition rate coefficient, $[\text{I}_0]_{\text{aq}}$ the aqueous phase SPS concentration, N_{Av} Avogadro's number, d_{d} the droplet (or particle) diameter, k_{tp} the rate constant for bimolecular termination, N_{p} the particle number per unit volume of the aqueous phases, and k_{des} the desorption rate coefficient. Values for the used parameters are collected in Table 3, a detailed description of the model to estimate $\bar{n}$ can be found in the original articles.^[42,43]

Values for $\bar{n}$ deviate significantly from 0.5 for particle diameters below 17 nm and above 180 nm. The very low water solubility of monomeric radicals and, therefore, the very low rate of radical desorption, extends this zero-one range to small droplet and particle diameters compared to more hydrophilic monomers such as STY or methyl methacrylate. Hence, the zero-one approach is justified for these particle diameters, and each particle or droplet is therefore assumed to contain at maximum 1 radical at any time.

3.3. Model Restrictions and Limitations

Simulations are based on a 20 wt% miniemulsion polymerization of LMA. Two important limitations hold for the modeling of a miniemulsion polymerization in general and for this model in particular. First of all, the efficiency of droplet nucleation ("which part of the droplets becomes a particle") is unknown. Therefore, two situations have been simulated where in one all droplets are nucleated at the

Table 3. Model input parameters based on lauryl methacrylate.

Parameter	Unit	Parameter	Unit
k_p	1.280 ^{a)}	ρ_{HD}	775
m_{mh}	1.001	$M_{w,mon}$	0.25442
χ_{mh}	0.38 ^{b)}	$M_{w,HD}$	0.22644
χ_{mp}	0.34 ^{b)}	f	0.6
χ_{hp}	0.37 ^{b)}	k_d	5.73×10^{-6} c)
γ	5×10^{-3}	k_{tp}	1×10^4
ρ_{pol}	929	k_{des}	1.23×10^{-6} d)
ρ_{mon}	870	N	500

a)Van Herk.^[36]; b)Van Krevelen.^[40]; c)at 60 °C for 0.02 M K₂S₂O₈/0.05 N NaOH.^[44]; d)Gilbert.^[45]

same time, while in the second situation droplets are nucleated throughout the reaction. Mathematically, this is an easy procedure, but the lack of experimental evidence reduces its predicting capability. Secondly, to the best of the authors knowledge, no direct knowledge on the droplet size distribution is available. The droplet size distribution imposes a more rigid problem. Since DLS only gives a poly value on the polydispersity, no reliable distribution can be extracted from it. Choi et al.^[15] have tried to provide graphical evidence for this distribution using freeze-fracturing combined with TEM, however, without fully satisfying results. Moreover, the droplet size distribution, measured at circumstances different from reaction conditions (i.e., room temperature, dilution) does not necessarily coincide with the miniemulsion at reaction conditions, since the latter is at higher temperatures much more prone to instability caused by coalescence and Ostwald ripening. Nevertheless, to obtain an acceptable estimation, the droplet size distribution is based on the droplet size distribution of an ODA miniemulsion, created using the formulation from Table 1. The even higher hydrophobicity and the presence of inhibitor (which could not be removed due to the solid state of the monomer at room temperature) might result in slightly larger droplets compared to LMA. The high melting temperature of ODA (≈ 32 °C) enforced us to perform the ultrasonication at 37 °C instead of 0 °C. The resulting miniemulsion consists, as a consequence of this high melting temperature, of solid monomer particles after cooling down to room temperature. This offered the possibility to measure the monomer particle size distribution using the PSDA technique, see Figure 5. This monomer particle size distribution can be adequately fit with an *F*-distribution ($N=500$), using a mean of 62 nm and parameters $v_1=40$ and $v_2=25$ (Figure 5).^[46] This distribution is used as a starting point for the simulations. In all simulations, a hexadecane volume fraction of 4% for each droplet has been used. To account for the effect of the

droplet diameter on the chemical potential, every simulation was preceded by an Ostwald ripening step to equilibrate all chemical potentials, resulting in different hydrophobe concentrations for differently sized droplets. Hexadecane and polymer are assumed to be confined within the droplet, so that only monomer can be exchanged between particles.

As a result of its limitations, the model cannot provide absolute values for the average particle size and the PSD, but it can predict the trend in the PSD development with conversion.

3.4. Model Results

Three different situations have been simulated: in the first one, every droplet is nucleated at the start of the polymerization ("instantaneous nucleation"). At every step, approximately 50% of the particles contain a radical and every particle captures on average the same number of

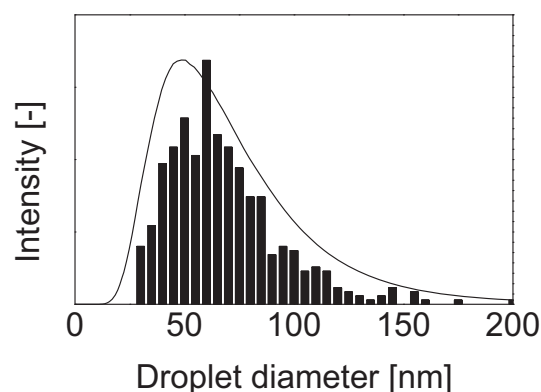


Figure 5. Droplet size distribution measured for an octadecyl acrylate miniemulsion using the PSDA technique (solid line) and the modeled droplet size distribution using an *F* distribution.^[46]

radicals. Since Figure 3a suggests that the final particle size and PSD is obtained around 30–45% conversion, a second simulation has been performed in which every droplet has an initial polymer volume fraction of 30% (“30% polymer”). Note that this is in fact nothing other than a seeded emulsion polymerization. The last simulation is based on the observations made by Miller et al.^[13] and the experimental results presented in this paper. Here, the nucleation period is assumed to be long and slow, whereas consecutive entries are supposed to be similar to the procedure described in the first two simulations (“prolonged nucleation”). The probability of the first radical entry was modeled to be linear with the particle diameter, the so-called diffusional entry model.^[47] Parameters were chosen such that around 60% conversion most of the droplets had been nucleated (Figure 6).

Results of the simulations are presented in Figure 7. The simulated conversion–time histories in Figure 7a demonstrate that the third simulation requires the longest time to reach full conversion, which is not surprising given the low number of nucleated particles at low conversion. The conversion–time histories of the other two simulations are nearly identical. Although the rate of polymerization is faster in the simulated polymerization without polymer due to the higher monomer concentration (Equation 8 and 9), the ratio of converted monomer to initial monomer

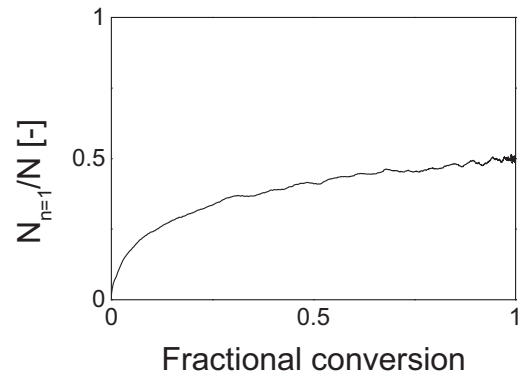


Figure 6. Simulated ratio of particles that contain 1 radical ($N_{n=1}$) to initial number of droplets (N) in the simulated miniemulsion polymerization with an non-instantaneous (or extended) nucleation period.

concentration is independent of initial polymer content, causing only minimal difference in the conversion–time histories. However, all three simulations proceed at a higher rate than was experimentally measured (Figure 1). The most probable cause for the difference between experimental observations and simulation results is the lower nucleation efficiency (“the number of droplets that become a particle”) in the experimental miniemulsion polymerization compared to the simulated polymerization. The rate of

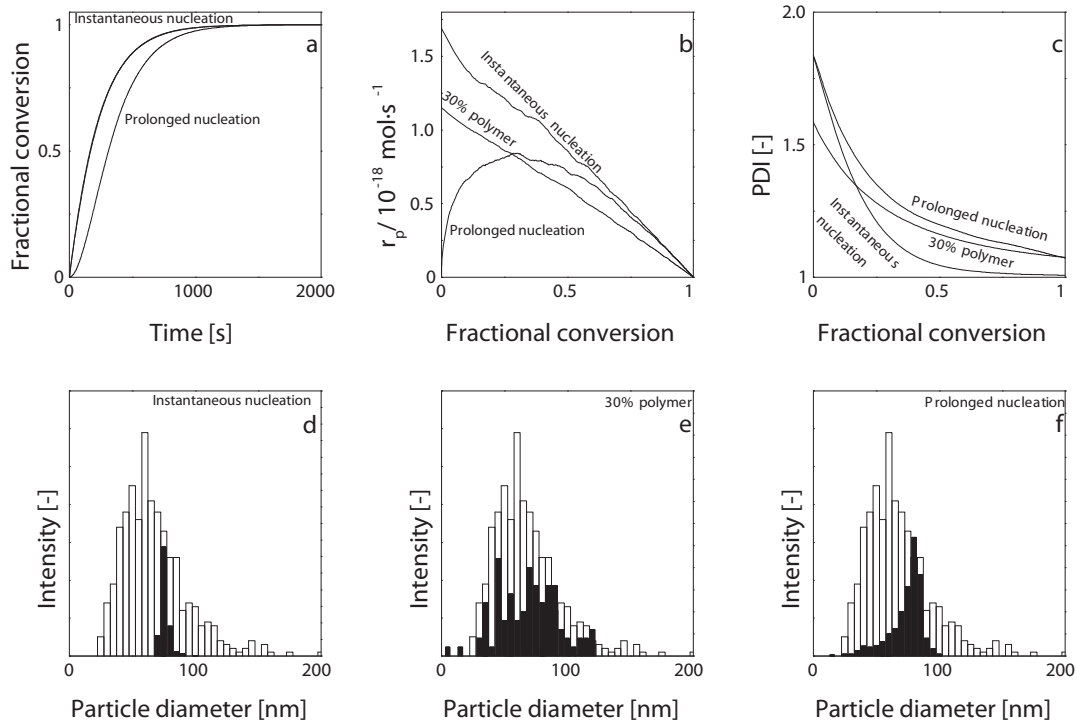


Figure 7. Results of the simulated miniemulsion polymerizations of lauryl methacrylate, displaying (a) conversion–time histories, (b) rates of polymerization, (c) polydispersities, and (d–f) droplet (white) and particle (black) size distributions.

polymerization (Figure 7b) for both simulations where all droplets become nucleated instantaneously shows a monotonously decreasing pattern. This is well explained by the decrease in monomer concentration in each particle, but it does not reflect the measured rate of polymerization in Figure 1 where we see a clear plateau in the polymerization rate for both LMA and its styrenic counterparts after a (short) first period of increase in rate. These features are only observed in the simulation where droplets are allowed to be non-nucleated up to high conversion. Although both the width and the starting point of this plateau can be manipulated by the choice of the model parameters and the chosen life time of the droplets, it supports the idea that droplets exist well throughout the miniemulsion polymerization. The gel effect at high conversion has not been included in the model and is therefore not visible in any of the simulations.

Finally, the polydispersities of all three simulations decrease with conversion as was observed experimentally (Figure 3). It is indeed confirmed that the narrowing of the PSD takes place mostly in the first half of the polymerization. Initiation of all the droplets at once results in a sharp decrease at low conversion and a PDI very close to 1 toward the end. A more gradual decrease is observed for the miniemulsion polymerization in the presence of non-nucleated monomer droplets. This is due to the slower depletion of the high end side of the droplet size distribution, as a consequence of the monomer feeding from the monomer droplets. It should be noted that at high conversion, particle viscosities will be very high, possibly imposing restrictions on monomer to escape to another particle, which accounts for the leveling off of the PDI in the experimental results. The miniemulsion polymerization in the presence of 30 vol% polymer shows the least decrease in PDI, as was expected. The lower initial PDI, compared to the two other simulations, is caused by the simulated Ostwald ripening prior to the start of the polymerization.

The model, however, fails to provide an explanation for the observed increase of the poly value at low conversion. Although it is tempting to attribute this to measurement errors, it has been observed at all three polymerizations and in many experiments not described here. The simulated results indicate that mass transfer from monomer droplets to nucleated particles cannot account for this effect. A possible explanation is the enhanced coalescence between droplets as well as between droplets and particles at reaction temperature, thereby both increasing the average diameter and reducing the number of droplets in the miniemulsion.

The simulated PSD are shown in Figure 7d–f. The very low PDI value of the simulation in which all droplets are nucleated instantaneously is reflected in the very narrow PSD, see Figure 7d. It confirms that a one-to-one copy of

droplets into particles with conservation of the original distribution is certainly not an intrinsic property of miniemulsion polymerization. Monomer has clearly been redistributed from large particles to small ones, resulting in the disappearance of both the high-end and the low-end side of the droplet size distribution. The presented particle size distribution and PDI are, for the limitations described before, indicative values for the used droplet size distribution, and it is therefore that they do not resemble the experimentally determined values. Although the PDIs of the two other simulations are almost the same (1.07), the resulting PSDs show remarkable differences. When polymer is included in the monomer droplets, the PSD displays some similarity with the original droplet size distribution, see Figure 7e. Again, the high-end side has disappeared, this time in favor of the low-end side, where we see particle diameters that are smaller than the smallest droplet diameters. On the other hand, when droplets are allowed to co-exist with particles (Figure 7f), a clearly defined peak in the PSD is observed. Again, the high-end size of the droplet size distribution has disappeared, but this time we find that the distribution is negatively skewed, albeit a positive skew in the droplet size distribution. This skew, which is to some extent also observed in the experimental PSDs of LMA miniemulsion polymerizations (Figure 2 and 3), is made up of droplets that have given up most of their monomer before nucleation has taken place. Please note that these observations are in agreement with earlier research.^[13,15] Density differences between monomer and polymer have been taken into account in the model (Table 3). However, these differences are too small to account for the observed differences in droplet and particle sizes.

The results obtained by simple model calculations provide some insight in mechanistic aspects of miniemulsion polymerization and show that typical observations made in miniemulsion polymerizations with aqueous phase initiation can be explained thermodynamically. Properties such as the width of the PSD of the final latex or the difference in measurements between (volume) average droplet and particle sizes are well simulated without having to refer to homogeneous nucleation. Lack of understanding of the nucleation process and input variables prevents a clear prediction of the final latex particle size and distribution. However, it is possible to model the trend.

4. Conclusions

The results of this work demonstrate that the particle size distribution in a miniemulsion polymerization of monomers with different water solubilities narrows throughout the polymerization when SPS is used as initiator. As a result of monomer chemical potential differences among droplets

caused by polymerization inside these droplets, monomer is transferred from large to small droplets. Using a simple thermodynamic model, the development of the particle size distribution throughout the course of a miniemulsion polymerization can be predicted. The final particle size distribution can be modeled best when monomer droplets are assumed to be present up to high conversion. This presence of monomer droplets has been confirmed experimentally, both by the presence of a plateau value in the rate of polymerization and by the growth of nucleated particles with conversion. Miniemulsion polymerizations using different amounts of initiator demonstrate that not all droplets become initiated. The results suggest that miniemulsion polymerizations do not always result in a one-to-one copy, preserving droplet number and distribution. Latex properties, such as the final particle size distribution, are governed by thermodynamics.

5. Abbreviations

AIBN	azobis-isobutyronitrile
AMBN	2,2'-azobis-(2-methyl butyronitrile)
DLS	dynamic light scattering
GC	gas chromatography
HD	hexadecane
LMA	lauryl methacrylate
ODA	octadecyl acrylate
PDI	polydispersity
PSD	particle size distribution
PSDA	particle size distribution analyzer
SC	sodium carbonate
SDS	sodium dodecyl sulfate
SPS	sodium persulfate
STY	styrene
TEM	transmission electron microscopy

6. Nomenclature

d_{avg}	average particle diameter
d_d	droplet or particle diameter
d_n	number average particle diameter
d_v	volume average particle diameter
f	efficiency factor
k_d	dissociation rate coefficient
k_{des}	desorption rate coefficient
k_p	propagation rate coefficient
k_{tp}	bimolecular termination rate coefficient
k_{tr}	chain transfer coefficient to monomer
m_{mh}	ratio molar volumes monomer and costabiliser
$\bar{n}$	average number of radicals/particle
n	actual number of radicals/particle

r_p	rate of polymerisation
t	time
z_{avg}	intensity average ("z average") diameter
γ	interfacial tension
ρ_{mon}	monomer density
ρ_{pol}	polymer density
ϕ_m	monomer volume fraction
ϕ_h	costabilizer volume fraction
ϕ_p	polymer volume fraction
χ_{mh}	Flory–Huggins interaction parameter of monomer and costabiliser
χ_{hp}	Flory–Huggins interaction parameter of polymer and costabilizer
χ_{mp}	Flory–Huggins interaction parameter of monomer and polymer
ΔG_m	monomer molar differential Gibbs-Free energy
M_w	molecular weight
N_{Av}	Avogadro's number
N_p	particle number per volume of water
P^i	monomer quantity in particle i
Q_{mon}^i	monomer molar quantity in particle i
R	universal gas constant
R_p	rate of polymerization (mol s^{-1})
T	temperature
V_{aq}	volume aqueous phase
$\bar{V}_m$	monomer molar volume
V_{mon}	volume monomer phase
V_{mon}^i	monomer volume in particle i
V_{pol}^i	polymer volume in particle i
$[I_0]_{\text{aq}}$	aqueous phase initiator concentration
$[M]_p$	monomer concentration in particle

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- [1] J. M. Asua, *Prog. Polym. Sci.* **2002**, 27, 1283.
- [2] K. Landfester, *Macromol. Rapid Commun.* **2001**, 22, 896.
- [3] F. J. Schork, Y. Luo, W. Smulders, J. P. Russum, A. Butté, K. Fontenot, *Adv. Polym. Sci.* **2005**, 175, 129.
- [4] J. Galindo-Alvarez, D. Boyd, P. Marchal, C. Tribet, P. Perrin, E. Marie-Bégué, A. Durand, V. Sadtler, *Colloids Surf. A* **2011**, 374, 134.
- [5] M. Goikoetxea, I. Beristain, R. J. Minari, M. Paulis, M. J. Barandiaran, J. M. Asua, *Chem. Eng. J.* **2011**, 170, 114.

- [6] G. Farzi, E. Bourgeat-Lami, T. F. L. McKenna, *J. Appl. Polym. Sci.* **2009**, *114*, 3875.
- [7] A. J. Back, F. J. Schork, *J. Appl. Polym. Sci.* **2007**, *103*, 819.
- [8] K. Tauer, A. M. Imroz Ali, U. Yildiz, M. Sedlak, *Polymer* **2005**, *46*, 1003.
- [9] J. R. Leiza, E. D. Sudol, M. S. El-Aasser, *J. Appl. Polym. Sci.* **1997**, *64*, 1797.
- [10] S. J. Bohórquez, J. M. Asua, *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 6407.
- [11] K. Landfester, N. Bechthold, S. Förster, M. Antonietti, *Macromol. Rapid Commun.* **1999**, *20*, 81.
- [12] S. Cheng, Y. Guo, P. B. Zetterlund, *Macromolecules* **2010**, *43*, 7905.
- [13] C. M. Miller, E. D. Sudol, C. A. Silebi, M. S. El-Aasser, *J. Polym. Sci. A: Polym. Chem.* **1995**, *33*, 1391.
- [14] C. M. Miller, E. D. Sudol, C. A. Silebi, M. S. El-Aasser, *J. Colloids Interface Sci.* **1995**, *172*, 249.
- [15] Y. T. Choi, M. S. El-Aasser, E. D. Sudol, J. W. Vanderhoff, *J. Polym. Sci. A: Polym. Chem.* **1985**, *23*, 2973.
- [16] C. T. Lin, J. M. Wu, C. S. Chern, *Colloids Surf. A* **2013**, *434*, 178.
- [17] U. Yildiz, K. Landfester, M. Antonietti, *Macromol. Chem. Phys.* **2003**, *204*, 1966.
- [18] R. Jovanovic, M. A. Dubé, *Macromol. Chem. Phys.* **2004**, *205*, 958.
- [19] T. G. T. Jansen, P. A. Lovell, J. Meuldijk, A. M. Van Herk, *Macromol. Symp.* **2013**, *333*, 24.
- [20] J. Ugelstad, H. Fløgstad, F. K. Hansen, T. Ellingsen, *J. Polym. Sci.* **1973**, *42*, 473.
- [21] M. Morton, S. Kaizerman, M. W. Altier, *J. Colloid Sci.* **1954**, *9*, 300.
- [22] I. A. Maxwell, J. Kurja, G. H. J. van Doremaele, A. L. German, *Makromol. Chem.* **1992**, *193*, 2065.
- [23] J. Ugelstad, P. C. Mørk, *Adv. Colloid Interface Sci.* **1980**, *13*, 101.
- [24] A. S. Kabalnov, A. V. Pertzov, E. D. Schukin, *Colloids Surf.* **1987**, *24*, 19.
- [25] A. Kabalnov, *J. Dispersion Sci. Technol.* **2001**, *22*, 1.
- [26] K. Tauer, *Polymer* **2005**, *46*, 1385.
- [27] S. Suriyarak, J. Weiss, *Colloids Surf. A* **2014**, *446*, 71.
- [28] J. Delgado, M. S. El-Aasser, *Makromol. Chem. Macromol. Symp.* **1990**, *31*, 63.
- [29] J. Delgado, M. S. El-Aasser, C. A. Silebi, J. W. Vanderhoff, J. Guillot, *J. Polym. Sci. B: Polym. Phys.* **1988**, *26*, 1495.
- [30] V. S. Rodriguez, J. M. Asua, M. S. El-Aasser, C. A. Silebi, *J. Polym. Sci. B: Polym. Phys.* **1991**, *29*, 483.
- [31] V. S. Rodriguez, J. Delgado, C. A. Silebi, M. S. El-Aasser, *Ind. Eng. Chem. Res.* **1989**, *28*, 65.
- [32] W. S. Rasband, *ImageJ*, U. S. National Institutes of Health, Bethesda, Maryland, USA, <http://imagej.nih.gov/ij/>, 1997–2012.
- [33] W. H. Lane, *Ind. Eng. Chem.* **1946**, *18*, 295.
- [34] C. S. Chern, T. J. Chen, *Colloids Surf. A* **1998**, *138*, 65.
- [35] F. J. Schork, A. Back, *J. Appl. Polym. Sci.* **2004**, *94*, 2555.
- [36] A. M. van Herk, *Macromol. Theory Simul.* **2000**, *9*, 433.
- [37] U. S. Satpathy, A. S. Dunn, *Br. Polym. J.* **1988**, *20*, 521.
- [38] C. S. Chern, H. T. Chang, *Polym. Int.* **2002**, *51*, 1428.
- [39] C. S. Chern, J. C. Sheu, *J. Polym. Sci. A: Polym. Chem. A* **2000**, *38*, 3188.
- [40] D. W. Van Krevelen, K. Te Nijenhuis, *Properties of Polymers: their Correlation with Chemical Structure, their Numerical Estimation and Prediction from Additive Group Contributions*, 4th ed., Elsevier Science, Amsterdam **2009**, p. 189–227.
- [41] F. K. Hansen, J. Ugelstad, *J. Polym. Sci. A* **1979**, *17*, 3069.
- [42] M. Nomura, K. Fujita, *Makromol. Chem. Suppl.* **1985**, *10/11*, 25.
- [43] S. Suzuki, K. Kikuchi, A. Suzuki, T. Okaya, M. Nomura, *Colloid Polym. Sci.* **2007**, *285*, 523.
- [44] E. Hakoila, *Ann. Univ. Turku. Ser. A* **1963**, *66*, 9.
- [45] R. G. Gilbert, *Emulsion Polymerization: A Mechanistic Approach*, Academic Press, London **1995**.
- [46] E. Kreyszig, *Advanced Engineering Mathematics*, 8th ed. John Wiley and Sons, Inc., New York **1999**, p. 1126.
- [47] J. Ugelstad, F. K. Hansen, *Rubber Chem. Technol.* **1976**, *49*, 536.