

On the Miniemulsion Polymerization of Very Hydrophobic Monomers Initiated by a Completely Water-Insoluble Initiator: Thermodynamics, Kinetics, and Mechanism

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ABSTRACT: Successful miniemulsion polymerizations of very hydrophobic monomers, such as lauryl methacrylate and 4-*tert*-butyl styrene, initiated by very hydrophobic (i.e., completely water-insoluble) lauroyl peroxide, are reported. Conversion-time histories, as well as final latex properties, for example, the particle size distribution, are different from similar miniemulsion polymerizations in the presence of water-soluble initiators. The observed differences can be attributed to the average number of radicals inside a miniemulsion particle; the system obeys Smith-Ewart case I rather than Case II kinetics. Albeit the pairwise generation of radicals in the monomer droplets, substantial polymerization rates are observed. Water, present in the droplet

interfacial layer, is supposed to act as chain transfer agent. The product of a chain transfer event is a hydroxyl radical, exit of this hydroxyl radical allows for the presence of single radicals in particles. The proposed mechanisms allow for agreement between initial droplet and final particle size distributions in miniemulsion polymerization initiated by lauroyl peroxide. © 2016 The Authors Journal of Polymer Science Part A: Polymer Chemistry Published by Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 2731–2745

KEYWORDS: calorimetry; lauroyl peroxide; miniemulsion polymerization; particle size distribution; radical exit

INTRODUCTION Miniemulsion polymerization has in the past 40 years evolved from a scientific curiosity to a widely applied polymerization technique for the lab-scale preparation of polymer latex.^{1–5} The number of industrial applications is also slowly growing.⁵ In miniemulsions, polymerization takes place upon the entry of radical species into preformed submicron monomer droplets rather than in monomer-swollen micelles. As a result of their large surface/volume ratio, micelles are much more likely to capture radical species than monomer droplets. Therefore surfactant concentrations in miniemulsion systems have to be well below the critical micelle concentration. However, the surfactant concentration should be high enough to provide sufficient stabilization against coalescence. To enhance the probability and rate of droplet nucleation, the monomer droplets in miniemulsion polymerization need to be much smaller than monomer droplets in conventional emulsion polymerization (i.e., 50–500 nm vs. 1–10 μ m). The addition of a small amount of costabilizer, which is a low molecular weight, highly water-insoluble component such as hexadecane, prevents Ostwald ripening, a pro-

cess by which droplets disappear by monomer diffusion from small to large droplets.^{6–8} By minimising both coalescence and Ostwald ripening, the droplet number and droplet size distribution can be kept constant for periods sufficiently long to be able to polymerize the miniemulsion droplets, yielding a latex with an average particle size comparable to the original droplet size. The control over the nucleation process and the number of reaction loci can result in reduced reactor fouling compared to conventional emulsion polymerization using the same formulation.⁹ However, in previous work we demonstrated that particle concentration and particle size distribution of the final latex do not necessarily agree with the droplet concentration and the droplet size distribution of the miniemulsion when water-soluble initiators are used.¹⁰ Different volumetric growth rates between nanoparticles result in a thermodynamic driving force for monomer transfer, thereby narrowing the resulting particle size distribution.

Historically, water-soluble initiators, usually in the form of salts, have been used in conventional and miniemulsion

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polymerization. These initiators introduce charged species to the latex, thereby having impact on polymer and latex properties, such as ionic strength, latex stability, and electrical conductivity. Unlike suspension polymerization, the use of noncharged oil-soluble initiators has never attracted much attention in conventional emulsion polymerization.^{11,12} It has been demonstrated that it is possible to reach complete conversion with oil-soluble initiators in conventional emulsion polymerization.^{13,14} However, polymerization rates are in general quite low and fouling is usually observed. The compartmentalized nature of miniemulsion droplets, however, paved the road for the use of these uncharged initiators in heterogeneous polymerization generating submicron particles. It is even debated that oil-soluble initiators could act as costabilizer.^{15,16} It would, by replacing hexadecane, minimize the postpolymerization treatment of the latex. With minimum initiator concentrations reported to be 1 wt % (with respect to monomer), no excess initiator is needed, which otherwise could have affected polymer properties. However, suppression of Ostwald ripening was only observed when lauroyl peroxide (water solubility 5.0×10^{-11} mol/dm³) was used.¹⁶ Initiators with lower monomer/water partition coefficients such as benzoyl peroxide and azobis-isobutyronitrile (AIBN) gave latex products with a bimodal particle size distribution or with very large particles.

EARLY WORK

In his review, Capek summarized the available literature up to 2001 on the use of oil-soluble initiators for miniemulsion polymerization as well as for conventional emulsion polymerization and microemulsion polymerization.¹³ In microemulsion polymerizations, droplets are thermodynamically stable and droplet sizes are usually below 50 nm. More recently, Yildiz et al. demonstrated that droplet and particle diameters agree for the miniemulsion polymerization of lauryl methacrylate with AIBN as the initiator.¹⁷ However, a deviation was observed with the use of water-soluble initiators (potassium persulfate or PEGA200, a poly(ethylene-glycol)-azo initiator). Jahanzaad and co-workers polymerized styrene droplets in the presence of a polyester resin and lauroyl peroxide.¹⁸ These authors showed that droplet sizes do not change much throughout polymerization. However, since their droplets contained high resin fractions and surfactant concentrations were high (8 g/dm³ sodium dodecyl sulfate), it would be more justified to mention it as a (homogenized) seeded polymerization. The same effects were observed when vinyl siloxane rubber was used as costabilizer in combination with AIBN.¹⁹ Using both AIBN and potassium persulfate as initiators, Cai et al. demonstrated that the number of particles in the final latex only equalled the number of droplets in the case of the monomer-soluble initiator.²⁰ Magnetic polymer particles were prepared by Mori et al., using water-soluble and monomer-soluble initiators, or a combination of both.²¹ It was demonstrated that the application of persulfates resulted in secondary particle formation and destabilization of the reacting miniemulsion, resulting in droplet coagulation. On the other hand, initiation in the monomer droplets resulted in a bimodal particle size distribution, with droplet and particle sizes being nearly the same. This

secondary nucleation was also the aim of investigation in a study towards seeded suspension polymerization with lauroyl peroxide and benzoyl peroxide.²² Surprisingly, the formation of new particles via secondary nucleation was more pronounced when the more hydrophobic lauroyl peroxide was used, which was attributed to the nucleation of monomer droplets used to swell the seed. Kohnle et al. applied high pressure to a miniemulsion of butadiene or a miniemulsion copolymerization of styrene and butadiene using various organic initiators at different temperatures.²³ Although copolymerizations seemed to result in narrower particle size distributions than (butadiene) homopolymerizations, a temperature dependency is also observed. To produce phosphonated polymers of methyl methacrylate (MMA) or styrene, Ziegler et al. used the hydrophobic initiator V59 (2,2'-azobis-(2-methylbutyronitrile) or AMBN) in a miniemulsion copolymerization with vinylphosphonic acid.²⁴ The polystyrene based copolymers that were formed demonstrated uniformity in particle size. The PMMA based copolymers displayed the presence of small particles next to a group of larger particles. This, combined with the calorimetric data, led to the authors' conclusion that the more hydrophilic MMA miniemulsion polymerization suffered from homogeneous polymerization. The miniemulsion polymerization of styrene, in the presence of a polymeric (cationic) surfactant, AIBN and at different pH values resulted in a rather broad particle size distribution, confirmed by transmission electron microscopy (TEM) and dynamic light scattering (DLS).²⁵ Average droplet and particle sizes were again constant throughout polymerization. Using pyrene and molecular rotors, the miniemulsion polymerization of MMA, initiated by AIBN, could be followed in-situ and real time.²⁶ The obtained fluorescence intensity spectra suggest that polymerization starts at the droplet-water interface, pointing to a mechanism where radicals enter the droplets rather than originating there. Finally, poly(butyl methacrylate) was grafted on ultrahydrophobic poly(dimethylsiloxane) macromonomers in miniemulsion polymerization.²⁷ These macromonomers acted both as grafting agent and costabilizer (or hydrophobe). When AIBN was incorporated as initiator, a stable latex was obtained with average particle sizes equal to monomer droplet sizes. The use of potassium persulfate, however, resulted in coagulation and phase separation of the macromonomer.

GENERATION OF SINGLE RADICALS

The main and still ongoing debate about the use of organic initiators in (mini)emulsion polymerization focuses on the location and fate of the formed radicals. Radicals are produced pairwise, either reversibly in the case of peroxides or irreversibly in the case of azo-initiators. Due to their confinement in the small monomer droplets or latex particles, the number of radicals will be either 0 or 2 per particle. According to the zero-one approach suggested by Smith and Ewart, the locally high radical concentration has to result in almost instantaneous termination.²⁸ On the other hand, molecular weights have been reported to be high, indicating relatively long growth times of polymer chains inside the particles.^{9,23,27} This contradiction can only be solved by assuming a mechanism that allows for the presence of a single

radical inside polymer particles. Generally, two 'schools' have developed in the past 25 years, stating that single radicals are created either from the initiator fraction that has partitioned to the aqueous phase (thereby acting as a water-soluble initiator) or that these single radicals are the result of radical exit and re-entry from and into polymer particles. The idea that single radicals are only formed in the aqueous phase was brought up by Nomura and Fujita, who claimed that the presence of a zero-one kinetics system inevitably has to imply aqueous phase initiation.²⁹ A similar conclusion was published shortly before by Choi et al., who based their conclusions on the retardation taking place when aqueous phase inhibitors were added.³⁰ This idea is supported by Luo et al., who attribute a significant contribution to the part of the initiator residing in the aqueous phase, especially with smaller particles.³¹ Their conclusions are based on the results obtained with aqueous phase radical scavengers. However, both studies show that polymerization takes place in the presence of an aqueous phase inhibitor, albeit at a lower rate, comparable to that of a bulk polymerization. This would then lead to a mechanism where radicals can desorb without reabsorption, rather than participating in bulk polymerization inside the monomer droplets. Choi et al., as well as Luo and co-workers; however, fail to prove either of these mechanisms by measuring the molecular weight, which should differ significantly for a 'bulk like' and an 'emulsion like' mechanism. On the other hand, a mechanism in which single radicals are generated by the exit of a radical fragment has been proposed.^{32,33} To calculate the average number of radicals per particle, a population balance was made, to be solved by an elaborate algorithm. This mechanism has been confirmed in AIBN initiated miniemulsion polymerizations using various monomer/water ratios.³⁴ The higher monomer/water ratio resulted in higher polymerization rates, while partitioning of the initiator was more to the organic phase. Improved computer facilities made application of this algorithm for solution of the radical population balance over the particle size distribution more feasible, while at the same time demonstrating that the fraction of the initiator in the aqueous phase only had a minor contribution to the polymerization process.³⁵ Rawlston et al. verified both experimentally and theoretically (by Monte Carlo simulations) the miniemulsion polymerization of styrene.³⁶ Using water-soluble inhibitors too, these authors showed that polymerization can be fully attributed to the creation of single radicals by radical desorption. This desorption process of initiator derived ('primary') radicals is mathematically formulated by Shang and coworkers using a two film model.³⁷ It is questionable, however, whether instationary radical desorption can be modeled using a stationary diffusion approach. Recently, Costa et al. presented a model to simulate the miniemulsion polymerization of butyl acrylate, MMA and styrene with organic initiators.³⁸ Using the aforementioned algorithm, the authors were able to predict the average number of radicals per particle for various particle diameters and at different conversions. However, the assumptions used, especially on the monodisperse nature of the monomer droplets, might have simplified the model too much.

In this paper, the results of miniemulsion polymerizations with lauroyl peroxide are presented. Water solubilities of the monomers in this work range from 3×10^{-2} mol/dm³ (styrene, 25 °C)³⁹ via 10^{-5} mol/dm³ (4-*tert*-butyl styrene)⁴⁰ and 5×10^{-8} mol/dm³ (lauryl methacrylate)⁴¹ to practically insoluble in water (octadecyl acrylate). To distinguish between both theories (i.e., generation of radicals in the aqueous phase or generation of single radicals by exit and re-entry), the water solubility of both the monomer and initiator are factors to be considered. The fraction of the ultrahydrophobic lauroyl peroxide that will partition to the aqueous phase is absolutely insignificant to initiate polymerization. Successful polymerization with lauroyl peroxide is therefore a clear indication against dominant radical formation in the aqueous phase. On the other hand, radical exit requires some water solubility of the exiting species. Historically, radical exit was solely attributed to monomer radicals, originating from chain transfer.^{29,42} More sophisticated models have been developed over the years, both based on chain transfer to monomer as well as on the desorption of other radical species.^{43–45} The exit of for instance initiator derived radicals has only recently been looked at as a possible contribution to (mini)emulsion kinetics.^{33,46} However, with the very low water solubilities of the monomer, radical partitioning will be fully to the organic phase, making exit of monomeric or oligomeric radicals highly unlikely. Since the lauroyl radical will display a water solubility that is even lower than for lauric acid (3.4×10^{-5} mol/dm³ at 30 °C), exit of initiator radical fragments is also unlikely.⁴⁷ A successful miniemulsion polymerization would therefore also be an argument against exit dominated kinetics. In this article, we propose a solution to this paradox. In addition to this we show, using thermodynamic principles, how the locus of initiation determines the broadness of the particle size distribution in a miniemulsion polymerization.

EXPERIMENTAL

Materials

Styrene (STY, >99%), 4-*tert*-butyl styrene (TBS, 93%), lauryl methacrylate (LMA, 96%), octadecyl acrylate (ODA, 97%) and hexadecane (HD, >99%) were all purchased from (Sigma-)Aldrich. Styrene was purified by distillation under reduced pressure, both 4-*tert*-butyl styrene and lauryl methacrylate were purified by passing these monomers over a column containing inhibitor remover (Sigma-Aldrich). Octadecyl acrylate ('stearyl acrylate') was used as received. Lauroyl peroxide (LPO, 97%) and sodium persulfate (SPS) were obtained from (Sigma-)Aldrich and BASF, respectively. Sodium dodecyl sulfate (SDS, >99%) was purchased from Merck. All these components were used as received. Deionized water (MilliQ standards) has been used throughout this work.

Procedure

The oil-soluble initiator and the hexadecane were dissolved in the monomer, according to the formulation given in Table 1. In a separate beaker, the SDS was dissolved in water. Both mixtures were transferred to a 1 dm³ container, agitated for at least 10 min and subjected to ultrasonication using a Branson CV33 horn controlled by a Sonics Vibracell VCX

750W at 65% output. Sonication was applied for 45 min while the emulsion was cooled using an ice bath.

After sonication, the miniemulsion was transferred to the Mettler-Toledo RC1e HP60 reaction calorimeter and consecutively purged for 30 min at room temperature using argon. This RC1e was equipped with a pitch blade impeller (6 blades, 45° pitch angle, 250 RPM), a calibration heater, a temperature sensor and an argon inlet. Reactions were performed in the isothermal mode at $(60.0 \pm 0.1)^\circ\text{C}$. Temperature as well as heat removal or supply were controlled by Icontrol 5.0 software. Directly after purging, the argon pressure inside the reactor was increased to 2.8 bar absolute, followed by a calibration (30 min, 5W calibration power) of the reactor contents performed at $(25.0 \pm 0.1)^\circ\text{C}$. Polymerization was started by quickly heating the reactor contents from 25 to 60 °C, a procedure that required approximately 5 min. In the case where a mixed initiator system of SPS and LPO was used, the SPS was dissolved in 20 mL water and mechanically added over 30 s while the reactor was heated. The point at which the reactor temperature was within 0.5 °C of the desired value was taken as the starting point of the reaction. After polymerization, the latex was cooled to 25 °C and the system was calibrated again. Monomer conversion was checked via residual monomer analysis by gas chromatography after ultrasonication, calibration, and polymerization using a Shimadzu GC-2010 equipped with a GC Flame Ionization Detector (FID) and a Varian Chrompack Capillary GC Column CP-SIL 5CB 25 $\times$ 0.25 $\times$ 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 calculated using both an internal (HD) and external (toluene) standard. The calorimetrically obtained time-conversion history was scaled to the final conversion measured by gas chromatography.

Since calorimetric measurements do not allow for the collection of samples throughout the reaction, the miniemulsion polymerization with LMA was repeated with quantities being 1/4th of the formulation presented in Table 1. This miniemulsion polymerization was performed in a 400 mL glass round bottom reactor, equipped with a four bladed impeller, a condenser and an argon inlet. The miniemulsion was purged with argon at room temperature for 30 min. Subsequently, the reaction vessel was suspended in a thermostated water bath at $(60.0 \pm 0.2)^\circ\text{C}$. The insertion moment of the reactor is regarded as the starting point of the polymerization. Samples were collected every 10 min, cooled and short stopped by the addition of a few mg hydroquinone. Conversion in these samples was measured using 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.

PARTICLE SIZE ANALYSIS

(cryo-)Transmission Electron Microscope (TEM) images were made using a FEI Tecnai 20 (type Sphera) TEM, operated

TABLE 1 Standard Miniemulsion Formulation for the Calorimetric Experiments

Component	Mass (g)
Water	800 (780)
Monomer	200
Hexadecane	8,0
Sodium dodecyl sulfate	4,0
Lauroyl peroxide	3.18 (3.18)
Sodium persulfate	(1.905)
Water for initiator	(20)

Numbers in brackets correspond with quantities in case of a mixed initiator system.

with a 200 kV LaB6 filament and a bottom mounted 1024 $\times$ 1024 Gatan CCD camera. Pictures were taken at a magnification of 7800. Particle size distributions were determined using ImageJ software.⁴⁸ Images were binarized using a luminance threshold. Consequently, particles were digitally distinguished from the noise, and the particle area was determined. The particle weight average diameter (D_w), the number average diameter (D_n) and the polydispersity (PDI) were calculated according to:

$$D_w = \frac{\sum n_i \cdot d_i^4}{\sum n_i \cdot d_i^3} \quad (1)$$

$$D_n = \frac{\sum n_i \cdot d_i}{\sum n_i} \quad (2)$$

$$\text{PDI} = \frac{D_w}{D_n} \quad (3)$$

in which d_i is the diameter of particle i and n_i the number of particles with size i . The volume mean diameter of the particles in a latex is calculated according to:

$$D_v = \sqrt[3]{\frac{\sum n_i \cdot d_i^3}{\sum n_i}} \quad (4)$$

This diameter is used in the calculation of the number of particles per unit volume of water:

$$N_p = \frac{6 \cdot V_{\text{mon}} \cdot \rho_{\text{mon}}}{\pi \cdot D_v^3 \cdot V_{\text{aq}} \cdot \rho_{\text{pol}}} \quad (5)$$

with V_{mon} and V_{aq} being the volumes of monomer and water in the reaction mixture, while ρ_{mon} and ρ_{pol} represent the densities of monomer and polymer, respectively. Scattering intensity based (D_z) droplet and particle diameters ('z-average') for the calorimetric measurements have been determined via dynamic light scattering using a Malvern Zetasizer Nano. Miniemulsions and final latex products were diluted in deionized water, containing 3.3 g/dm³ SDS at $(20.0 \pm 0.1)^\circ\text{C}$. When styrene miniemulsions were measured, this surfactant solution was saturated with styrene. The Zetasizer has an internal filter

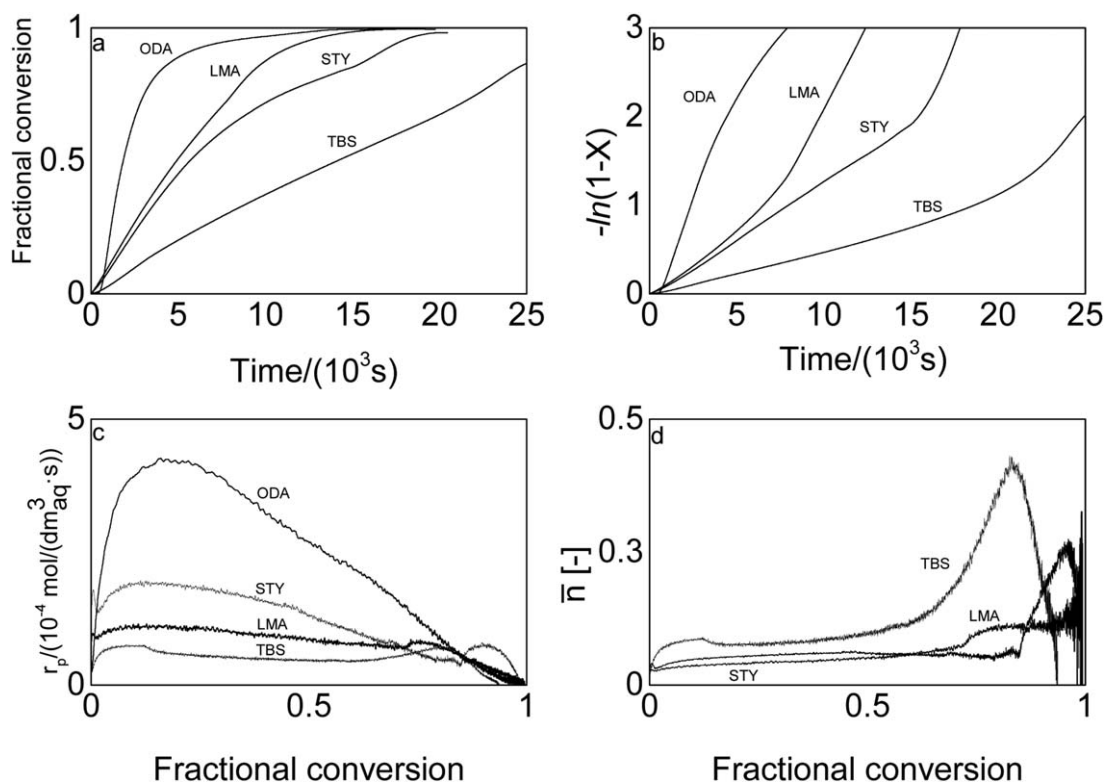


FIGURE 1 Calorimetric data for the miniemulsion polymerizations of styrene (STY), 4-tert-butyl styrene (TBS), lauryl methacrylate (LMA) and octadecyl acrylate (ODA), initiated by lauroyl peroxide. Displaying conversion-time histories (a,b), rate of polymerization (c), and average number of radicals per particle, calculated via eq 6 (d), using IUPAC propagation rate coefficients.⁴⁹

which is automatically adjusted to give a count rate of ~ 250 kcounts/s. Reported values are average values for three runs comprising 16 measurements of 20 seconds each, determined by the cumulants method. Scattering intensity based average droplet and particle sizes for the LMA miniemulsion polymerization in the glass reactor have been determined by dynamic light scattering using a Brookhaven Instruments BI-9000AT correlator with a Brookhaven BI-200SM goniometer set to a scattering angle of 90° and a 20 mW HeNe laser (632.8 nm wavelength). Samples were diluted with a $3.3 \text{ g}/\text{dm}^3$ SDS solution to give a count rate of ~ 150 kcounts/s at the detector and, after temperature equilibration, were subjected to 10 successive analyses of 1 min each. The jacket temperature was held at $(25.0 \pm 0.1)^\circ\text{C}$, whereas the exact jacket temperature was used as input when analysing the data using Brookhaven Particle Sizing Software v3.72 to obtain individual values of the particle diameter for each of the 10 measurements. Reported values are an average of these measurements, the standard deviation was typically ~ 2 nm. Particle sizes were determined according to the cumulants method. Blank measurements indicated that SDS micelles had no detectable influence on the results for both types of dynamic light scattering devices. For both sets of experiments, the width of the distribution is indicated by the so-called *poly*.

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 50–1000 nm.

Electron spray ionization–time of flight (ESI-ToF) measurements were performed on a Waters Synapt G1 ESI-ToF in V mode. For these analyses, latex samples were precipitated in acetone, after which the extract phase was analyzed both in positive and negative mode. Acquisition times were usually between 2 and 2.5 min.

RESULTS AND DISCUSSION

Experimental Results

Figure 1 shows the conversion-time histories for the miniemulsion polymerizations of styrene (STY), 4-tert-butyl styrene (TBS), lauryl methacrylate (LMA) and octadecyl acrylate (ODA), all initiated by lauroyl peroxide (LPO). Rates of polymerization as measured by reaction calorimetry, as well as the average number of growing chains per particle ($\bar{n}$), are also collected in Figure 1.

All miniemulsion polymerizations showed complete colloidal stability during the reaction, that is, no fouling was observed. The results in Figure 1 clearly demonstrate that, despite the arguments given in the introduction on the use of only hydrophobic components with respect to the radical distribution, it is possible to successfully polymerize very

TABLE 2 Weight Average (D_w) and Number Average (D_n) Particle Diameters, Volume Mean Average Particle Diameters and Polydispersity Index, Determined by Transmission Electron Microscopy (TEM) of Latex Products Resulting from Miniemulsion Polymerizations of Styrene (STY), 4-*tert*-Butyl Styrene (TBS), Lauryl Methacrylate (LMA), and Octadecyl Acrylate (ODA), as well as Intensity Average (D_z) Particle and Droplet Diameters and Poly Values Determined by Dynamic Light Scattering

	D_w (nm)	D_n (nm)	D_v (nm)	PDI (–)	D_z Droplets (nm)	Poly (–)	D_z Particles (nm)	Poly (–)
STY	98	64	75	1.54	155 ^a	0.396 ^a	108	0.087
TBS	149	104	120	1.43	151	0.128	151	0.060
LMA	155	89	105	1.73	164	0.117	168	0.102
ODA	–	–	–	–	170	0.144	162	0.134
STY ^b	94	91	92	1.03	128	0.132	92	0.017
TBS ^b	104	102	103	1.02	149	0.136	109	0.028
LMA ^b	121	110	113	1.10	176	0.111	127	0.014

For reasons of completeness, results of miniemulsion polymerizations with sodium persulfate are included as well.

^a Multiple peaks detected, probably erroneous measurement caused by droplet dissolution.

^b Initiation by sodium persulfate. Results extracted from Jansen et al.¹⁰

hydrophobic monomers in miniemulsion using LPO as the sole initiator.

The overall rates of polymerization for miniemulsion systems initiated by LPO are undoubtedly lower than for similar miniemulsion systems initiated by sodium persulfate.¹⁰ Moreover, the conversion-time histories of these LPO initiated polymerizations do not reflect the typical S-shape often observed in (mini)emulsion polymerizations with (long) nucleation periods and in the presence of monomer droplets. Instead, the conversion-time history resembles more a bulk polymerization. This is confirmed by Figure 1(B), which displays the negative logarithm of the fraction of unreacted monomer ($1 - X$) versus time.

In the case of a (pseudo) first order bulk polymerization, this should give a linear relation between $\ln(1 - X)$ and time, as is clearly demonstrated for LMA, STY, and TBS for conversions up to 65% or higher. Above this conversion, a gel effect occurs and as a result, the radical concentration is no longer constant and the pseudo first order assumption is no longer obeyed. For aqueous phase initiated miniemulsion polymerizations instead, the presence of droplets, and therefore a constant monomer concentration inside the polymer particles, results in a pseudo zeroth order behavior in the conversion-time histories.¹⁰ The bulk-like behavior for LPO initiated miniemulsion polymerization is also visible from the rate of polymerization [Fig. 1(c)]. For all polymerizations, a continuous decrease of the polymerization rate after a steep initial rise can be observed. Albeit this continuous decrease is less pronounced for LMA and TBS than for ODA and STY, the difference with the plateau (or even increase) in the polymerization rates measured for aqueous phase miniemulsion polymerization is apparent.¹⁰ Bulk behavior in (mini)emulsion polymerization is usually indicative for either a Smith–Ewart case I or case III situation, in which the average number of radicals ($\bar{n}$) per particle is considerably lower or higher than 0.5.²⁸ Using the rate of polymerization, $\bar{n}$ has

been calculated using eq. 6 for all polymerizations except the one employing ODA, for which no average particle diameter could be determined by transmission electron microscopy (TEM), see Figure 1(d).

$$r_p = \frac{k_p \cdot [M]_p \cdot \bar{n} \cdot N_p}{N_{Av}} \quad (6)$$

in which r_p is the rate of polymerization (mol/(dm³_{aq} s)), $[M]_p$ the monomer concentration in the particles and N_{Av} Avogadro's number. The number of particles per dm³ water, N_p , is calculated using eq 5 and the average particle diameters collected in Table 2. The IUPAC values for the propagation rate coefficients of LMA (1280 dm³/(mol s)) and STY (341 dm³/(mol s)) at 60 °C have been used.⁴⁹ For TBS, no value for k_p was available. This value is estimated to be equal to the value of STY. All three miniemulsion polymerizations display values for $\bar{n}$ well below 0.5, indicating a polymerization dominated by radical exit. Note that the use of the number average diameter instead of the volume mean diameter would result in estimated $\bar{n}$ values approximately half the values reported in Figure 1(d).

Particle Size Distributions

The particle and droplet diameters, measured by dynamic light scattering (DLS) and (cryo-)TEM are collected in Table 2. Examples of the (cryo-)TEM pictures and the derived particle size distributions (PSD) are presented in Figure 2. Unfortunately, the cryo-TEM images generated from the ODA miniemulsions showed significant particle deformation (i.e., nonspherical particles). As it was unclear whether this was an artefact of the microscopy measurements or whether this represented the actual particles, no reliable particle size distribution could be extracted from it.

It is apparent from Figure 2 and the measured polydispersities that the PSDs of the latex products are significantly broader than their aqueous phase initiated counterparts.¹⁰

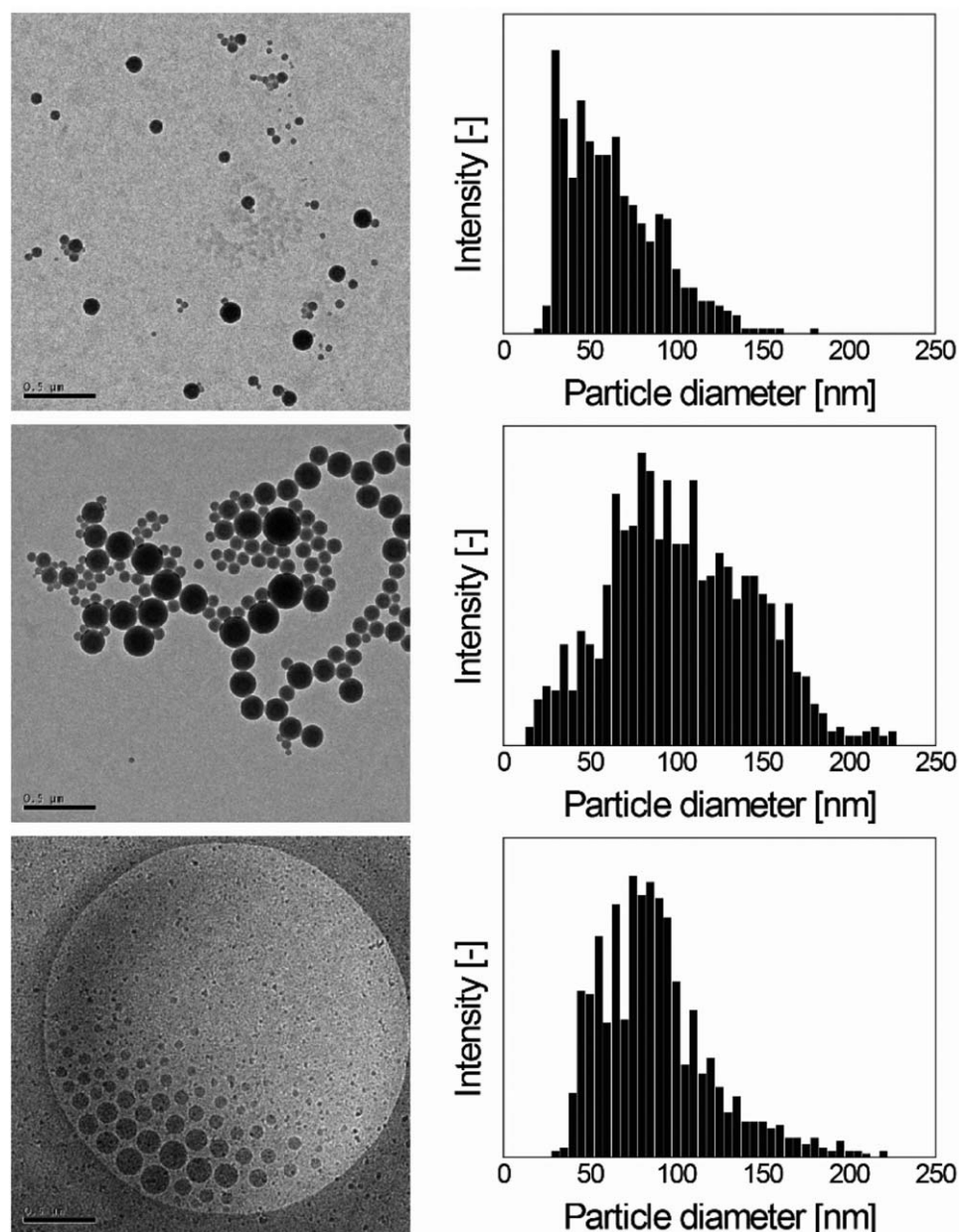


FIGURE 2 Particle size distributions, obtained from (cryo-)transmission electron microscopy, for miniemulsion polymerizations with styrene (top), 4-tert-butyl styrene (center) and lauryl methacrylate (bottom), all initiated by lauroyl peroxide. Number of particles counted: 586 (styrene), 1150 (4-tert-butyl styrene), 1111 (lauryl methacrylate).

The droplet diameters and their *poly* values, measured for both TBS and LMA, agree very well with the values measured on similar miniemulsions that have been polymerized using sodium persulfate, see Table 2. This gives a strong indication that the miniemulsions before polymerization in both experiments, that is, with sodium persulfate or LPO as initiator, were comparable, despite the presence of LPO that could contribute as hydrophobe.

The high values measured for the weight average (D_w) and intensity averaged (D_z) diameters should not be misinterpreted and result in the false conclusion that the number of

particles is lower than obtained with sodium persulfate; in fact, the volume mean particle diameter (D_{avg}) indicates that the number of particles is even slightly higher in the case of LPO initiation. This also indicates that the lower polymerization rates for LPO initiation are purely an effect of the number of radicals per particle and not of the particle number.

Although it is doubtful to draw conclusions, based only on DLS measurements, the agreement between miniemulsion droplet and latex particle diameters as well as the high *poly* values for the LPO initiated miniemulsion polymerizations is striking. This gives rise to the idea that a direct translation

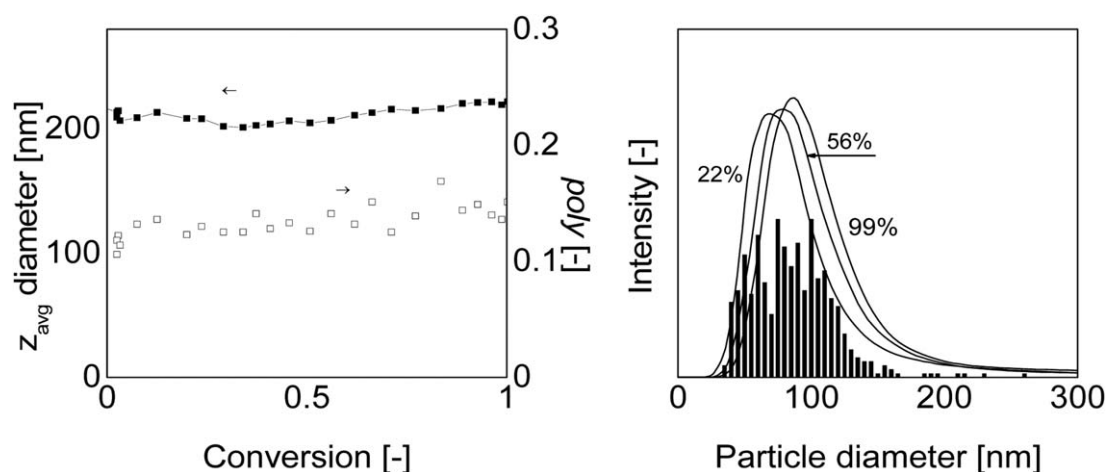


FIGURE 3 Particle size analysis of an LPO initiated miniemulsion polymerization of lauryl methacrylate at various conversions, showing the scattering intensity based average diameter D_z (■) and poly value (□) determined via dynamic light scattering (left) and the particle size distribution measured by the particle size distribution analyzer (various conversions, solid lines) and cryo-transmission electron microscopy (final conversion, 505 particles counted) (right).

of monomer droplets into polymer particles, the so called one-to-one copy, is possible in miniemulsion polymerization, at least with respect to the particle size distribution.

To confirm this observation, the particle size of an LMA miniemulsion polymerization ($D_z = 208$ nm, $poly = 0.095$) has been followed at various stages of the polymerization using dynamic light scattering. This reaction was carried out in a round bottom flask with all chemicals at 1/4th of the quantities given in Table 1. At regular intervals in the polymerization, the D_z and $poly$ value have been determined. Next to this, the particle size distribution has been determined using the Particle Size Distribution Analyzer (PSDA). This PSDA equipment is the particle size equivalent of size exclusion chromatography, in which latex particles are separated based on particle size by means of a packed column consisting of porous beads. DLS does not distinguish between monomer droplets and polymer particles, whereas the PSDA does by its inability to measure droplets. The combination of these techniques therefore offers the possibility to differentiate between droplets and particles. Figure 3 displays the obtained results.

The data collected in Figure 3 confirm that conservation of the particle size (distribution) is indeed achieved. The constant D_z and constant $poly$ value suggest that no significant *net* monomer transfer takes place during the reaction. Moreover, the overlap of the PSDA measurements at different conversions suggests that monomer droplets are transformed into particles at a very early stage in the polymerization. However, the discrepancy between the particle size distribution obtained from PSDA and cryo-TEM analysis, visible for the large particle diameters, suggests that the PSDA software algorithm might give slight deviations from the actual particle size distribution for polydisperse samples. The here presented particle size measurements are in good agreement with published results on systems initiated by AIBN,^{21,25,50}

LPO,¹⁸ and even with results of the microemulsion polymerization of butyl acrylate with LPO and dibenzoyl peroxide.⁵¹

The small difference in the measured intensity average droplet diameter between this measurement and the calorimetric measurement is due reaction inhibition at the start of the experiment, which has resulted in extensive Ostwald ripening. The reported droplet diameter therefore corresponds to the diameter at which first polymerization was detected. Although this implies that both miniemulsions cannot be regarded to be identical copies of each other, this in our opinion does not invalidate the conclusions presented here, as conservation of droplet size distribution with conversion is clearly confirmed by this measurement.

Combined Initiator System

At this point, it is clear that a miniemulsion polymerization initiated by lauroyl peroxide or other oil-soluble initiators results in a relatively slow polymerization process and yields a coagulum-free latex with a particle size distribution that seems to be not significantly different from the droplet size distribution obtained directly after emulsification. On the other hand, the particle diameters in Table 2 also indicate that miniemulsion polymerizations with sodium persulfate (or in general aqueous phase initiators) result in a relatively fast polymerization process, yielding a latex with a narrow particle size distribution. This of course only applies when the droplet and particle diameters are in the range where Smith-Ewart case II kinetics is obeyed. To find out which initiator is dominant in the polymerization, a miniemulsion polymerization of TBS in the presence of both sodium persulfate and LPO was performed. The scattering intensity diameter of this miniemulsion was 146 nm, with a $poly$ value of 0.101. Both initiators were added according to the quantities given in Table 1, and consequently, the actual amount of initiator in the system was doubled compared to formulations for polymerizations with only LPO or sodium

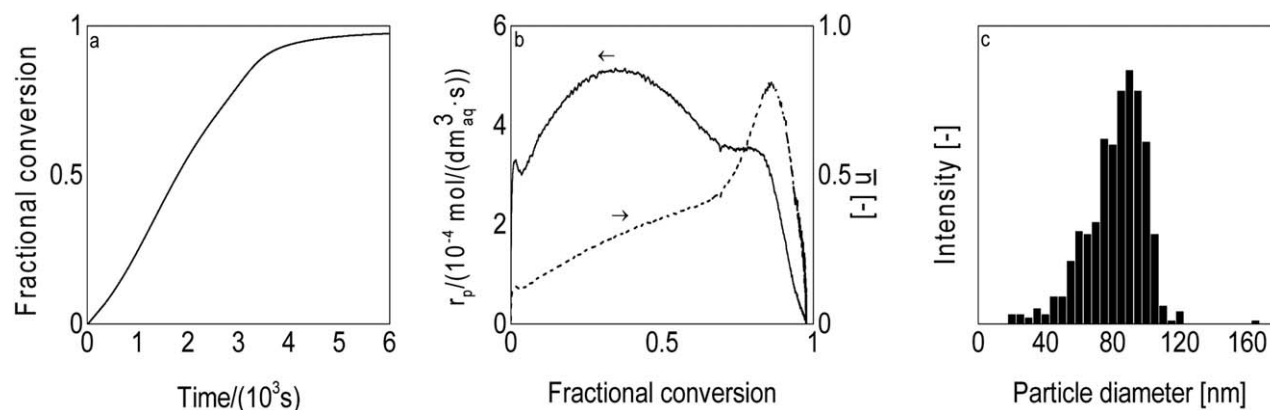


FIGURE 4 Reaction characteristics of a 4-*tert*-butyl styrene miniemulsion polymerization in the presence of both lauroyl peroxide and sodium persulfate, formulation see Table 3: (a) the conversion-time history, (b) the rate of polymerization (solid line) and average number of radicals per particle ($\bar{n}$, dashed line), and (c) the particle size distribution of the final latex, measured by transmission electron microscopy (616 particles counted).

persulfate. Contrary to the polymerizations with only sodium persulfate, no sodium carbonate was added as pH buffer. The combination of buffering agent and LPO resulted in polymerization during the ultrasonic treatment, at a polymerization rate higher than observed at reaction temperature. The results of the miniemulsion polymerization with a combined initiator system are displayed in Figure 4.

The high rate of polymerization, the relatively high average number of radicals per particle and the narrow PSD (scattering intensity diameter of 98 nm with a *poly* of 0.028) indicate that the aqueous phase initiation is dominant in this system. Nevertheless, there are also a few minor differences visible. The rate of polymerization is slightly higher than in any of the polymerizations with only one type of initiator. The more profound difference can be found in the particle size distribution. Figure 4(c) shows that all the large droplets have lost at least a part of their monomer to growing smaller particles, as is usually the case with aqueous phase initiation. However, a tail of very small particles is present. These small particles have not been observed when only sodium persulfate was used.¹⁰ The average particle diameter, measured by TEM and calculated according to eq 4, is smaller with a combined initiator system than in any other polymerization (85 vs. 104 nm in case of sodium persulfate and even 120 nm with LPO, see Table 2). These smaller particle sizes and, as a consequence, higher particle numbers for the combined initiator system explain the higher rate of polymerization. Both initiators were present in equal molar quantities. Dissociation rate coefficients at 60 °C for LPO ($1.2 \times 10^{-5} \text{ s}^{-1}$)⁵² and sodium persulfate ($\approx 6 \times 10^{-6} \text{ s}^{-1}$)⁵³ are of the same order of magnitude. It is, therefore, unlikely that the radical generation rate per unit volume of miniemulsion is significantly larger for any of the initiators. The efficiency of the radical generated in the aqueous phase must therefore be higher, which is fully understandable from the cage effect being relevant for LPO in the organic phase. This cage effect, the effect that radicals are produced pairwise in the submicron monomer droplets, results in almost instantane-

ous (ir)reversible termination of these radicals. Radicals formed in the continuous, more abundant aqueous phase instead, have a much larger chance of staying alive and giving entry in monomer droplets. These radicals, therefore, dominate the miniemulsion polymerization, resulting in Smith-Ewart case II kinetics. Large droplets, regardless whether nucleation has taken place, will supply monomer to growing smaller particles, thereby reducing their diameter. The nonuniform volumetric growth rates of the differently sized particles in a case II kinetic regime form a thermodynamic driving force for monomer transport from large to small droplets. The non-nucleated droplets, however, will not completely disappear, contrary to polymerizations with only aqueous phase initiation. The continuously increasing concentration of LPO inside these droplets, as a result of the disappearance of monomer, will increase the probability of a droplet to particle transition, resulting in the presence of small polymer particles in the final latex product. Note that these observations to some extent agree with the observations reported by Chern et al. who used a combination of AIBN and sodium persulfate, but noticed a slightly lower polymerization rate compared to sodium persulfate only, probably caused by a reduced particle number.⁵⁰

Nucleation Mechanism

The results of the experiment with a combination of LPO and sodium persulfate demonstrate the importance of the aqueous phase initiator concentration. The much higher efficiency of the aqueous phase generated radicals allows the reduction of the water-soluble initiator concentration to give a nucleation rate comparable to monomer phase initiation. Therefore, organic initiators with significant partitioning towards the aqueous phase, such as AIBN, might well operate from both aqueous phase, as well as from the organic phase. LPO, however, does not partition towards the aqueous phase significantly, and consequently, resides therefore almost completely in the droplet phase. When an initiator molecule dissociates, it generates two radicals that are confined in the small droplet volume. Classic Smith-Ewart

theory predicts that the local radical concentration is so high that instantaneous termination takes place provided that the droplets or particles are not too large. For larger particles, multiple radicals can co-exist. This, however, is not the case in any of our miniemulsion systems, given the very low values observed for $\bar{n}$ and the submicron particle diameters in miniemulsions. An accurate measurement of the molecular weight of the synthesized polymers consisting of LMA or TBS was unfortunately not possible due to a combination of insufficient solubility of the polymers in any eluent and the too small difference in refractive index between THF and polymer. Nevertheless, a provisional size exclusion chromatography (SEC) measurement on the STY polymer showed a weight average molecular weight of approximately 1×10^6 g/mol. This high molecular weight is in agreement with results published by Alduncin et al. and clearly demonstrates that the presence of more than one radical in a particle is very unlikely.⁹ The only other possibility to have successful polymerization is to arrive at a situation with an odd number of radicals in one particle. This can be accomplished by radical exit from the droplet and particles. The fate of the exiting radicals is unknown, but generally three possibilities can be sketched: aqueous phase termination, entry in other particles and re-entry. Aqueous phase termination would occur when the time constant of radical termination is much smaller than the time constant of radical entry in a particle:

$$\frac{1}{k_{t, \text{aq}} \cdot [R]_{\text{aq}}} \ll \frac{1}{2 \cdot \pi \cdot D_{\text{aq}} \cdot d_d \cdot f \cdot N_p} \quad (7)$$

in which $k_{t, \text{aq}}$ is the second order (aqueous phase) termination rate coefficient ($\text{m}^3/(\text{mol s})$), $[R]_{\text{aq}}$ the aqueous phase radical concentration, D_{aq} the aqueous phase diffusion coefficient (m^2/s), d_d the droplet or particle diameter, and f an efficiency factor. We do not distinguish at this point between the origin of the radicals (oxygen derived, initiator derived), although the applied argon atmosphere excludes most of the oxygen derived radicals. For an order of magnitude estimation, $k_{t, \text{aq}} \approx 1 \times 10^5 \text{ m}^3/(\text{mol s})$, $D_{\text{aq}} \approx 1 \times 10^{-9} \text{ m}^2/\text{s}$, $d_d \approx 1 \times 10^{-7} \text{ m}$ and $N_p \approx 4 \times 10^{20} \text{ particles/m}^3_{\text{aq}}$, giving a necessary aqueous phase radical concentration of 2.5 mM when complete efficiency is assumed. Although this is only an order of magnitude calculation, the high value necessary for the radical concentration predicts that aqueous phase termination is not the most likely fate of exiting radicals, leaving entry in particles as the only option left.

When we assume on the other hand that radicals are fully absorbed by surrounding particles after these radicals have escaped from a particle or droplet, the polymerization will inevitably end up in a zero-one kinetic regime, provided that particles are small enough to prevent pseudo bulk kinetics. Particles are then consecutively switched 'on' and 'off' by entry and exit events. As a consequence, the dissociation of an LPO molecule will result in chain termination and start the growth of a new chain simultaneously. Therefore, LPO dissociation can be regarded as a chain transfer event. The low values measured for $\bar{n}$, however, indicate that it is unlikely to have complete reabsorption. This would suggest

that aqueous phase termination might play some role. Another, more exotic mechanism, might be that radicals after exit will preferentially re-enter in the particle that they escaped. With sufficient time between exit and re-entry, chain growth takes place. The escaped radical species is hydrophobic and is assumed to remain in the proximity of the particle. If the time constant of re-entry is much smaller than the time constant of exit, the average number of radicals per particle will be below 0.5.

Radical Origin

In a system, consisting of very hydrophobic monomers and initiators, the origin of the exiting radical is not unambiguous. The exiting radical can be either a monomeric radical, an initiator fragment ('primary radical') or a secondary radical. Initially, the reactivity of a primary radical was assumed to be so high that the time constant of exit was regarded to be much larger than the time constant for propagation. Consequently, exiting radicals were deemed to originate from radical transfer.⁵⁴ The mathematically derived equation for the desorption coefficient is:⁵⁵

$$k_{\text{des}} = \frac{12 \cdot D_{\text{aq}} \cdot \delta \cdot k_{\text{tr}}}{M \cdot d_d^2 \cdot k_p} \quad (8)$$

With

$$\delta = \left(1 + \frac{6 \cdot D_{\text{aq}}}{M \cdot D_p}\right)^{-1} \quad (9)$$

in which D_{aq} and D_p are the monomer diffusion coefficients in the aqueous and the particle phase respectively, k_{tr} is the rate coefficient for chain transfer to monomer, k_p the propagation rate coefficient, and M the radical partition coefficient between organic and aqueous phase ($\text{m}^3_{\text{aq}}/\text{m}^3_{\text{mon}}$). This approach has been criticized and several adjustments have been proposed, taking into account possible reabsorption of radicals.^{43–45} However, eq 8 emphasizes the water solubility of the exiting radical, as it shows a direct dependency on the partition coefficient. The estimated partition coefficient of LMA ($7 \times 10^7 \text{ m}^3_{\text{aq}}/\text{m}^3_{\text{mon}}$)⁴¹ is five orders of magnitude larger than for instance the partition coefficient of STY (0.3×10^3). The high partition coefficient of LMA makes it unlikely that exit is initiated by chain transfer to monomer.

For the prediction of the rate of exit of initiator radicals, it is necessary to distinguish the different radicals that can be formed upon dissociation of lauroyl peroxide. The simple dissociation into two acyclic radicals (Fig. 5) is the simplest yet reversible method of radical formation:

However, acyl radicals are well-known for irreversibly releasing carbon dioxide (Fig. 6):⁵⁶

A nucleophilic attack of a hydroxyl anion (OH^-) on a carbonyl atom could, via subsequent proton abstraction from water, result in the formation of a peracid which can dissociate by releasing a hydroxyl radical.⁵⁷

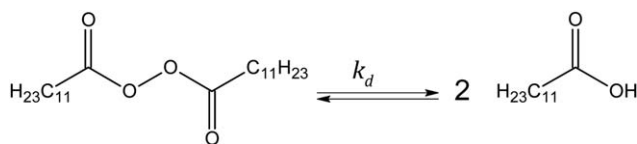


FIGURE 5 Simple dissociation of lauroyl peroxide into two acyclic radicals.

The reaction given in Figure 7 is assumed to take place at the monomer/water interface, and would give an explanation why the presence of a buffering agent (pH approximately 10.4) resulted in high polymerization rates with ice water cooling during ultrasonication, whereas no polymerization was observed during ultrasonic treatment in the absence of a buffering agent (pH approximately 6.4). The created peracid is assumed to dissociate relatively easy, producing an $\text{HO}^\bullet$ radical that has sufficient water solubility to exit the particle.

The very low water solubility of any radical that can be formed in the dissociation of lauroyl peroxide, except for the ones created upon the addition of hydroxyl ions, does not make exit of these hydrophobic radicals probable. As stated previously, the water solubility of the primary peroxide radicals is expected to be between lauric acid ($3.4 \times 10^{-5} \text{ mol/dm}^3_{\text{aq}}$) and simple undecane or dodecane (approximately 0.2 ppb or $1\text{--}2 \times 10^{-8} \text{ mol/dm}^3_{\text{aq}}$).⁵⁸ Hence, an alternative exit mechanism has to be postulated. In this mechanism, we assume that the primary carboxyl radicals will be located preferentially at the droplet/water interface. Although their carboxylic head is uncharged, unlike lauric acid, they might still have amphiphilic properties. This gives these radicals the opportunity to create hydroxyl radicals via hydrogen abstraction by the reaction given in Figure 8, resulting in hydrophobic lauric acid and a relatively hydrophilic hydroxyl radical that can escape from a particle:

The hydroxyl radical formed is very well capable of escaping the droplet or particle and can enter another droplet/particle. A method in which direct hydrolysis of the peroxide takes place, resulting in a peracid and lauric acid (Fig. 9), is deemed to be insignificant due to the low reactivity of the peroxide bond compared to the radical and the location of the peroxide molecule. If the reaction represented Figure 9 was the main source of hydroxyl radicals, polymerization would occur during sonication and miniemulsion storage as well, but this has not been observed.

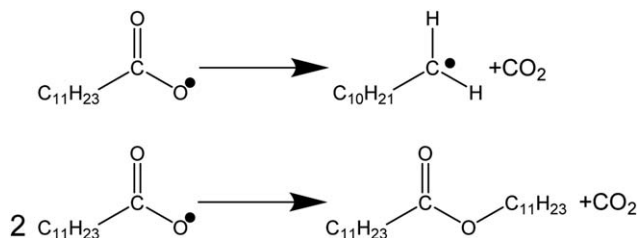


FIGURE 6 Carbon dioxide release from lauroyl peroxide primary radicals.

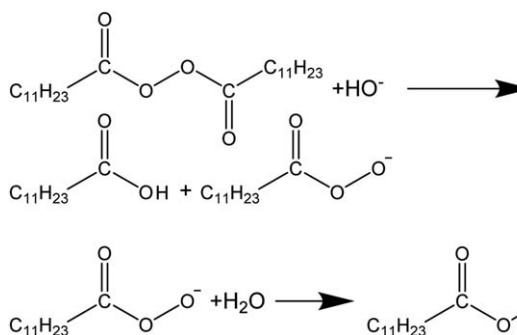


FIGURE 7 Formation of a peracid of lauroyl peroxide by interfacial reaction with hydroxyl ions.

A direct proof of the presence of hydroxyl end-groups (or peroxy end-groups) via for instance matrix-assisted laser desorption ionization time of flight (MALDI-ToF) or electro spray ionization (ESI) mass spectroscopy has unfortunately not been possible to date. The recovery of a sufficient amount of oligomers, which make up only a very small fraction of the total polymer mass, as well as the solubility of these oligomers in a suitable solvent has hampered a MALDI-ToF analysis so far. Moreover, the ability of these oligomers to 'fly' and the poor resolution between oligomer and matrix material (or, in case of ESI, monomer contaminations) prevented a clear proof. An indirect proof can be given although. For this, a latex prepared by miniemulsion polymerization of ODA in the presence of LPO was extracted with acetone and the extract phase was analyzed by ESI in the negative mode; see Figure 10.

Since most of the polymer precipitated, the extract phase only contains residual monomer, initiator and perhaps some oligomers. Figure 10 shows a clear peak at 199.2 Da, which corresponds with deprotonated lauric acid. The presence of a molecule, having the same molecular mass as lauric acid, is indicative for a mechanism as proposed by the reactions presented in Figures 7 and 8. The resulting hydroxyl radical is then the escaping radical, bringing down the number of radicals in a monomer droplet or polymer particle from two to one. The hydroxyl ion is sufficiently hydrophilic to exit, but simultaneously sufficiently hydrophobic to give entry into a particle without having to form a so-called z-mer in the aqueous phase.⁵⁹ Nevertheless, the evidence for the mechanism postulated is insufficient for a complete proof and supporting information is still necessary.

To calculate the probabilities of all these events, the time constants for each event can be estimated and compared. For propagation, initiator dissociation and monomeric radical desorption, the time constants are given by eqs (10–12):

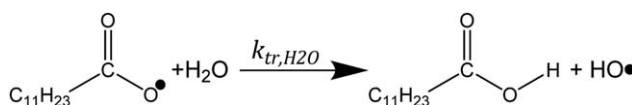
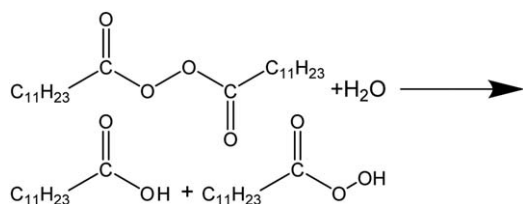


FIGURE 8 Radical transfer from primary radicals to water.

**FIGURE 9** Direct hydrolysis of lauroyl peroxide.

$$t_p = \frac{1}{k_p \cdot [\text{LMA}]_0} = 2.3 \times 10^{-4} \text{ s} \quad (10)$$

$$t_d = \frac{1}{k_d} = 8.3 \times 10^4 \text{ s} \quad (11)$$

$$t_{\text{des}} = \frac{1}{k_{\text{des}}} = 3.3 \times 10^7 \text{ s} \quad (12)$$

Calculations are based on a dissociation rate coefficient k_d of $1.2 \times 10^{-5} \text{ s}^{-1}$, a propagation rate coefficient of $1280 \text{ dm}^3/(\text{mol s})$ and an LMA bulk concentration of 3.41 mol/dm^3 .^{41,49,52} The desorption coefficient of a monomeric radical is given by eq 8. Assuming a particle diameter of 100 nm, a partition coefficient M of $7 \times 10^7 \text{ m}^3_{\text{aq}}/\text{m}^3_{\text{mon}}$, an aqueous phase diffusion coefficient of $1.2 \times 10^{-9} \text{ m}^2/\text{s}$ and a chain transfer coefficient (to monomer) equal to the chain transfer coefficient of butyl methacrylate (i.e., $2 \times 10^{-5} \text{ m}^3/(\text{mol s})$), the time constant for desorption of monomeric radicals is $3.3 \times 10^7 \text{ s}$.⁶⁰

To give an expression for the desorption coefficient of initiator radicals, two situations need to be distinguished: dissociation in a particle containing zero radicals and dissociation in a particle containing one radical. In the latter case, termi-

nation between the polymeric radical and one of the newly formed radicals leaves one single initiator radical in the particle. In analogy with the approach proposed by Asua et al. for monomeric radicals, we can derive the following equation for the radical exit rate coefficient, assuming complete reabsorption of the radicals:⁴²

$$k_{\text{des}}^{\text{ini}'} = 1 \cdot k_d \cdot \frac{[\text{LPO}]_0}{\left[\frac{\bar{n}}{N_{\text{Av}} \cdot V_p}\right]} \cdot \frac{12 \cdot D_{\text{aq,pr}}}{M_{\text{ini}} \cdot d_p^2} \cdot \frac{1}{k_p \cdot [\text{LMA}]_0} \quad (13)$$

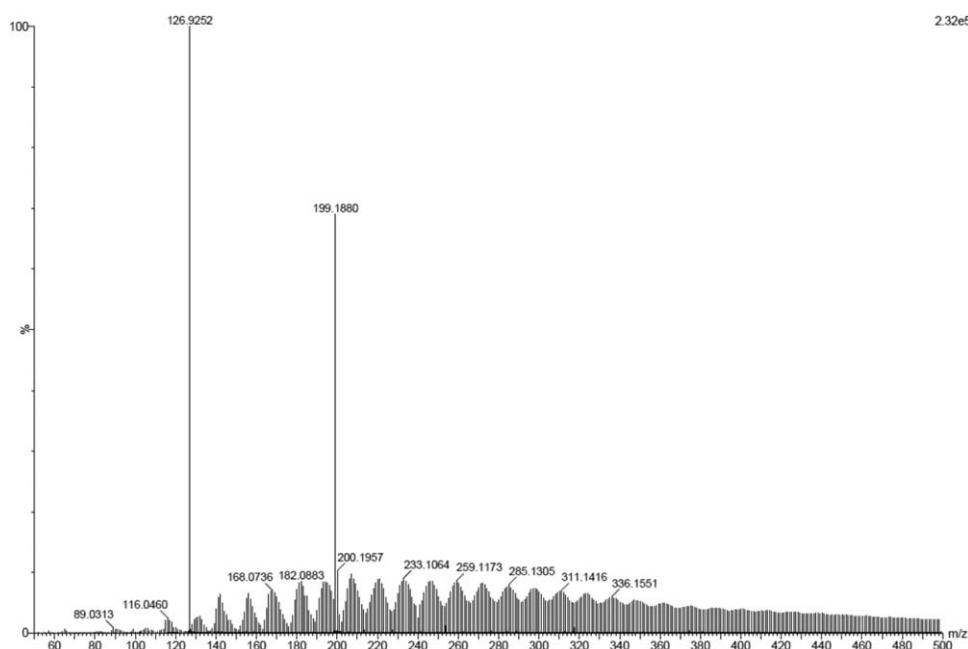
in which V_p is the particle volume, M_{ini} the partition coefficient for initiator radicals, $D_{\text{aq,pr}}$ the primary radical diffusion coefficient in water ($1.2 \times 10^{-9} \text{ m}^2/\text{s}$) and $[\text{LPO}]_0$ the initiator concentration in the droplets. When no radical is present when dissociation takes place, we have to modify eq 13 for the presence of two radicals and the possibility of termination:

$$k_{\text{des}}^{\text{ini}''} = 2 \cdot k_d \cdot \frac{[\text{LPO}]_0}{\left[\frac{\bar{n}}{N_{\text{Av}} \cdot V_p}\right]} \cdot \frac{12 \cdot D_{\text{aq}}}{M \cdot d_p^2} \cdot \frac{1}{k_p \cdot [\text{LMA}]_0 + \frac{k_t}{N_{\text{Av}} \cdot V_p}} \quad (14)$$

The total desorption rate coefficient for initiator desorption is then the sum of both individual rates, that is, eqs 13 and 14. When the time constant of termination, $\frac{N_{\text{Av}} \cdot V_p}{k_t}$, is much larger than the time constant of propagation, $\frac{1}{k_p \cdot [\text{LMA}]_0}$, the expression $\frac{k_t}{N_{\text{Av}} \cdot V_p}$ can be neglected and the total desorption rate coefficient simplifies to:

$$k_{\text{des}}^{\text{ini}} = 3 \cdot k_d \cdot \frac{[\text{LPO}]_0}{\left[\frac{\bar{n}}{N_{\text{Av}} \cdot V_p}\right]} \cdot \frac{12 \cdot D_{\text{aq,pr}}}{M_{\text{ini}} \cdot d_p^2} \cdot \frac{1}{k_p \cdot [\text{LMA}]_0} \quad (15)$$

Using a value of 0.1 for the average number of radicals $\bar{n}$ and an initiator fragment partition coefficient M_{ini} of $7 \times$

**FIGURE 10** Electro spray ionisation-time of flight (ESI-ToF) mass spectrum of an octadecyl acrylate latex extracted by acetone, measured in negative mode.

$10^7 \text{ m}_{\text{aq}}^3/\text{m}_{\text{mon}}^3$, the time constant for exit by initiator radicals is $4.3 \times 10^4 \text{ s}$. Radical transfer to initiator, followed by initiator decomposition, which is another way of producing initiator radicals, has not been taken into account here, since transfer constants to lauroyl peroxide are (close to) zero.⁵²

The desorption rate coefficient for the radical transfer that produces a hydroxyl radical, as proposed by Figure 8, can be derived in a similar way to the desorption coefficient for initiator-derived radicals:

$$k_{\text{des}}^{\text{OH}} = \frac{3 \cdot k_{\text{tr,H}_2\text{O}} \cdot [\text{H}_2\text{O}]_{\text{int}}}{k_{\text{p}} \cdot [\text{LMA}]_0} \cdot \frac{12 \cdot D_{\text{aq}}}{M_{\text{OH}} \cdot d_{\text{p}}^2} \quad (16)$$

in which $k_{\text{tr,H}_2\text{O}}$ is the radical transfer coefficient to water, $[\text{H}_2\text{O}]_{\text{int}}$ the water concentration at the interface and M_{OH} the partition coefficient for hydroxyl radicals between the organic and the aqueous phase. This reaction is assumed to take place at the particle/water interface, hence the interfacial water concentration. Moreover, parameter estimation for the transfer coefficient to water as well as for the partition coefficient of the hydroxyl radical are not straightforward. For a conservative estimation, we assume the transfer constant to be equal to the transfer constant of MMA to water, $2.5 \times 10^{-6} \text{ m}^3/(\text{mol s})$.⁵² The partition coefficient is assumed to be $0.1 \text{ m}_{\text{aq}}^3/\text{m}_{\text{mon}}^3$. The interfacial concentration of water is assumed to be equal to the bulk concentration, $5.5 \times 10^3 \text{ mol/m}^3$. Using these values, the calculated time constant for desorption of a hydroxyl radical is 0.8 s , which is orders of magnitude smaller than any of the other time constants for desorption, making this the most likely desorption event. However, the uncertainty in the values of the parameters results in a large margin for the actual value of the desorption coefficient. On the other hand, since we assume this reaction to take place at the interface, the diffusion length is not equal to the particle diameter anymore, but is reduced to the thickness of the interfacial layer, which would reduce the time constant even further.

Effect of Radical Distribution on Particle Size Distribution

The resulting uniform particle size distribution, obtained in a miniemulsion polymerization initiated by an aqueous phase initiator, was described as an artefact of a Smith–Ewart case II situation for these initiators.¹⁰ Equal reaction rates per particle (mol/s), that is, the same value for $\bar{n}$ in every droplet regardless of its size in droplets (particles) of different sizes result in monomer concentration differences between these differently sized particles with conversion, resulting in mass transfer from larger to smaller particles. Values for $\bar{n}$, calculated from the observed rates of polymerization in the experiments with LPO [see Fig. 1(d)] suggest Smith–Ewart case I kinetics instead. Note that for Smith–Ewart case I kinetics, the rate of polymerization is approximately proportional to the volume of the particle, that is, equivolumetric reaction rates between differently sized particles.^{61,62}

To prove the dependency of the average number of radicals on the droplet or particle volume in the miniemulsion polymeriza-

tions with hydrophobic monomers and initiators described above, we use the calculation method for $\bar{n}$ previously derived by Mørk et al. These authors modified the approach to calculate $\bar{n}$, originally derived for aqueous phase initiators, so that it was applicable for organic initiators.⁶³ It was demonstrated that the calculation for organic initiators is comparable to that of aqueous phase initiators. The herewith derived Ugelstad plot, predicting the value of $\bar{n}$ as function of various particle properties, can be found in the original article.⁶³

Following the approach suggested by Mørk et al., determination of α_{p} , which is defined as the ratio of radical generation and bimolecular termination inside the particles gives access to the value of $\bar{n}$:

$$\alpha_{\text{p}} = \frac{2 \cdot f \cdot k_{\text{d}} \cdot [I]_{\text{p}} \cdot N_{\text{Av}}^2 \cdot \pi \cdot d_{\text{d}}^3}{6 \cdot k_{\text{tp}} \cdot N_{\text{p}}} \quad (17)$$

where $[I]_{\text{p}}$ is the initiator concentration inside the droplet or particle and k_{tp} the second order termination rate coefficient inside a particle.

The insufficient knowledge of critical parameters, such as the termination rate coefficient k_{tp} as well as the efficiency f does not permit an accurate calculation of the $\bar{n}$ value. However, using the same values for N_{p} and d_{d} as before, combined with an initiator dissociation coefficient of $1.2 \times 10^{-5} \text{ s}^{-1}$,⁵² a particle phase termination coefficient of $1 \times 10^5 \text{ m}^3/(\text{mol s})$ and an efficiency factor of 0.1 , the value for α_{p} can be estimated to be around 3×10^{-4} . This value is found to be in the region where $\bar{n}$ is proportional to the particle or droplet volume, regardless of particle size, radical desorption rate, and radical reabsorption.

It was possible to arrive at the same conclusion by a more analytical approach. For that, the equation describing the average number of radicals as proposed by Mørk et al. is used.⁶³

$$\bar{n} = (\alpha - K \cdot \alpha_{\text{p}} + Y \cdot \alpha^2)/m \quad (18)$$

where K is the initiator partition coefficient between aqueous and monomer phase, and is inversely related to the initiator partition coefficient M_{LPO} (i.e., $K = \frac{1}{M_{\text{LPO}}}$, $K = 0$ means completely water insoluble). Y denotes the ratio of aqueous phase termination and radical absorption in polymer particles (i.e., $Y = 0$ means complete reabsorption of escaped radicals). The parameter m represents the ratio of radical desorption and bimolecular termination:

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

Assuming no water solubility of the initiator ($K = 0$) and no aqueous phase termination ($Y = 0$), eq 18 reduces to:

$$\bar{n} = \frac{\alpha}{m} \quad (20)$$

The ratio of absorption versus aqueous phase termination, α , is given by:⁶³

$$\alpha = \frac{\rho_a \cdot \pi \cdot d_p^3 \cdot N_{Av}}{6 \cdot N_p \cdot k_{t,aq}} \quad (21)$$

in which the rate of radical absorption, ρ_a , is given by:

$$\rho_a = k_a \cdot [R]_{aq} \cdot N_p \quad (22)$$

The rate coefficient for radical absorption is given by:⁶⁴

$$k_a = 2 \cdot \pi \cdot D_{aq} \cdot d_p \cdot N_{Av} \cdot f_a \quad (23)$$

with f_a being the absorption efficiency. Equation 8 gives the rate coefficient for desorption, necessary in calculating the ratio of radical desorption and bimolecular termination in the particles (eq 19). Substituting eqs 8, 19, and (21–23) in eq 20 gives an expression for the average number of radicals per particle as function of the third power of the particle diameter:

$$\bar{n} = \beta \cdot d_d^3, \quad \beta = \frac{\pi \cdot N_{Av} \cdot f_a \cdot [R] \cdot M \cdot k_p \cdot k_{t,p}}{6 \cdot k_{t,aq} \cdot k_{tr} \cdot \delta} \quad (24)$$

Note that, instead of eq 8, also the expressions for the desorption coefficients derived in eqs 15 or 16 could have been used. This would then have given a slightly different expression for β , depending on the LPO concentration or the interfacial water concentration and with different chain transfer coefficients.

These calculations demonstrate the dependency of $\bar{n}$ on the particle volume. Since the monomer conversion rate in a particle is dependent upon $\bar{n}$, this implies that throughout polymerization the ratio of monomer to polymer will only differ slightly between particles, contrary to polymerizations initiated by an aqueous phase initiator. From the Morton Equation describing the chemical potential of the monomer in the droplets and particles (eq 25), it is apparent that, with similar monomer fractions in all particles, the monomer chemical potential difference between particles at any point in the polymerization is marginal and is mostly due to a difference in the interfacial tension.⁶⁵

$$\frac{\Delta G_m}{RT} = \ln(\phi_m) + (1 - m_{mh}) \cdot \phi_h + \phi_p + \chi_{mh} \cdot \phi_h^2 + \chi_{mp} \cdot \phi_p^2 + \phi_h \cdot \phi_p \cdot (\chi_{mh} + \chi_{mp} - \chi_{hp} \cdot m_{mh}) + \frac{4 \cdot \gamma \cdot V_m}{RT \cdot d_d} \quad (25)$$

In eq 25, ϕ_m , ϕ_h , and ϕ_p represent the volume fractions of monomer, hydrophobe, and polymer respectively, m_{mh} the ratio of molar volume between monomer and hydrophobe, χ_{mh} , χ_{mp} , and χ_{hp} the various Flory–Huggins interaction coefficients between monomer, hydrophobe, and polymer, γ the droplet–water interfacial tension and V_m the monomer molar volume.

This in turn results in a very small driving force for net mass transfer between individual particles which allows the miniemulsions to retain their particle size distributions. Thus, this phenomenon, which is often described as a property of miniemulsion polymerization, is in fact a special situation determined by thermodynamic restrictions.

CONCLUSIONS

The miniemulsion polymerization of very hydrophobic monomers such as lauryl methacrylate and 4-*tert*-butyl styrene, initiated by lauroyl peroxide, has been investigated. In miniemulsion polymerizations with oil-soluble initiators, two mechanisms for the generation of single radicals are usually assumed: aqueous phase dissolution of the initiator and radical transfer to monomer followed by exit of the monomeric radical. By choosing monomers and initiator with negligible water solubilities, it was possible to exclude both mechanisms. The successful miniemulsion polymerisation of styrene, 4-*tert*-butyl styrene, lauryl methacrylate and octadecyl acrylate, yielding a clear, fouling-free latex, indicated that there should be a competitive mechanism of nucleation. It is suggested that the hydrolysis of a lauroyl peroxide radical, resulting in lauric acid and a hydroxyl radical, would generate radicals that are sufficiently water soluble to allow for radical exit.

It has been shown that all miniemulsion polymerizations described in this study obey Smith–Ewart case I kinetics up to high conversion. The low initiator efficiency results in low average numbers of radicals inside the particles (i.e., $\bar{n} \leq 0.15$), typical for case I kinetics in which $\bar{n}$ is proportional to the particle volume. This proportionality enables every particle to be polymerized at an equivolumetric rate, thereby creating no significant differences in monomer thermodynamic activity between differently sized particles. The minimization of the driving force for net mass transfer between particles allows droplets and particles to retain their size throughout the polymerization, which is demonstrated experimentally. The same miniemulsion polymerization, that after polymerisation gave a very narrow particle size distribution when sodium persulfate was used, gave a relatively broad particle size distribution in the presence of lauroyl peroxide. The results presented in this work show that the thermodynamic activities inside monomer droplets and polymer particles are a key factor in miniemulsion polymerization.

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