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Particle Formation in RAFT-Mediated Emulsion Polymerization: A Calorimetric Study

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Summary: *Ab initio* RAFT-mediated semi-continuous emulsion polymerizations with controlled monomer feed have been studied by reaction calorimetry. This online monitoring technique provided detailed information about the onset of the nucleation period in semi-batch processes for emulsion polymerization of styrene and n-butyl acrylate. The reactions were carried out under controlled radical polymerization conditions by employing amphipathic macro-RAFT agents of various degrees of surface activity. For n-butyl acrylate as well as for styrene the more surface active polymeric macro-RAFT agents led to higher initial polymerization rates. Polymerizations with hydrophobic macro-RAFT agents also adapted more quickly to an increased monomer feed than polymerizations with hydrophilic macro-RAFT agents.This points to the presence of more particles when a hydrophobic macro-RAFT agent is used. Hydrophobic macro-RAFT agents demonstrated to be promising for producing latex products with a proper control of particle number and particle size distribution.

Keywords: controlled radical polymerization; emulsion polymerization; macro-RAFT agent; particle nucleation; reaction calorimetry

Introduction

Emulsion polymerization processes are frequently applied for the production of rubbers, coatings and many other products. The generally slightly or moderately water-soluble monomers are mainly present in the monomer droplets which are dispersed in the aqueous phase. The actual polymerization, which is generally initiated by a water-soluble initiator, proceeds in the latex particles, which are much smaller than the monomer droplets. Particles are formed by entry of surface active radicals in micelles, homogeneous nucleation or (undesired) droplet nucleation.The product of an emulsion polymerization is a colloidally stable dispersion of submicron particles in water. A comprehensive description of the mechanistic aspects of emulsion polymerization has been given by Gilbert.[1]

The rate of polymerization per unit volume of the aqueous phase (R_p) depends on the monomer concentration in the latex particles ($[M]_p$), the time average number of free radicals per particle ($\overline{n}$) and the propagation rate coefficient for the monomer (k_p). Since every particle is basically a mini-reactor in an emulsion polymerization, the overall polymerization rate generally increases with the number of particles per unit volume of the aqueous phase (N_p). Equation (1) gives an expression for the rate of polymerization:

$$R_p = \frac{k_p \cdot [M]_p \cdot \overline{n} \cdot N_p}{N_{Av}} \left[\frac{mol}{dm_w^3 \cdot s}\right] \qquad (1)$$

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N_{Av} stands for Avogadros number. Note that $[M]_p$ may depend on the particle diameter. N_p may change as a result of secondary nucleation or coagulation. Also the apparent k_p will change with conversion. For a constant volume batch process the conversion rate is given by Equation (2):

$$\frac{dX}{dt} = \frac{k_p \cdot [M]_p \cdot \bar{n} \cdot N_p \cdot V_{water}}{N_{M0} \cdot N_{Av}} \left[\frac{1}{s}\right] \tag{2}$$

In Equation (2) X, N_{M0} and V_{water} stand for the fractional monomer conversion, the initial amount of monomer in the reaction mixture and the water volume, respectively. The heat flow rate (Q_r) released during the emulsion polymerization reaction is given by Equation (3):

$$Q_r = R_p \cdot (-\Delta H_r) \cdot V_{water}[\text{Watt}], \tag{3}$$

where ΔH_r is the heat of polymerization. Values for the reaction enthalpies of radical polymerization of vinyl monomers determined by calorimetry in the liquid state for the monomers studied in the work presented in this paper, i.e. styrene and n-butyl acrylate, have been reported as respectively between 68.5 and 73 kJ/mol (at 26.9 °C[2,3]) and 78 kJ/mol (at 74.5 °C[2,4]). The variations in the polymerization enthalpies are due to differences in reaction phases, temperature and environment of the measurements. So using literature values obtained for a system as close as possible to the system under investigation[5] is recommended. Monitoring the generated heat flow (Q_r) during a reaction with a reaction calorimeter gives access to polymerization rates, see Equation (3). Note that heat effects of initiation, bimolecular termination and transfer are negligible since the number of propagation steps is orders of magnitude larger than the number of all other reactions. Successful use of a reaction calorimeter has been reported for monitoring emulsion polymerization kinetics,[5–16] nucleation effects,[17–19] control of molecular weight[20] and other processes.[21–23]

Emulsion polymerization processes demand for relatively large amounts of surfactant. In addition molecular weight control is rather limited. RAFT (Reversible Addition Fragmentation Transfer) mediated emulsion polymerization can perhaps cope with the disadvantages of relatively high amounts of surfactant and the relatively poor molecular weight control. The principle of controlled radical polymerization by RAFT[24] is displayed in Figure 1.

Figure 2 shows the concept of RAFT mediated *ab initio* emulsion polymerization.

Starting with a proper RAFT agent, first a hydrophilic block is formed. Subsequently polymerization of a hydrophobic monomer at hydrophilic block is performed leading to a surface active species. Self assembly leads to particle formation and the controlled polymerization of the hydrophobic monomer proceeds in these freshly formed particles. After nucleation the controlling RAFT agent is directly at the locus of polymerization, so transport issues of the RAFT agent from the monomer droplets to the particles through the aqueous phase are avoided. This paper describes the results of particle formation in RAFT-mediated emulsion polymerization of n-butyl acrylate or styrene. Reaction calorimetry was used to monitor the course of the polymerization. The measured heat flow during controlled feed *ab initio* emulsion polymerization gives insight into particle formation by self-assembly of the amphipathic macro-RAFT agents. Macro-RAFT agents of different hydrophobicity have been studied. Hydrophilic blocks consist of acrylic acid. The building blocks of the hydrophobic part are n-butyl acrylate or styrene.

Experimental Part

Amphipathic macro-RAFT agents were prepared according to the scheme given in Figure 3.

Chemicals

The RAFT agent 2-{[(butylsulfanyl)-carbonothioyl]sulfanyl}propanoic acid, see Figure 3, was used as supplied by Dulux, Australia. The procedure for synthesis of this RAFT agent is described in literature.[25,26]

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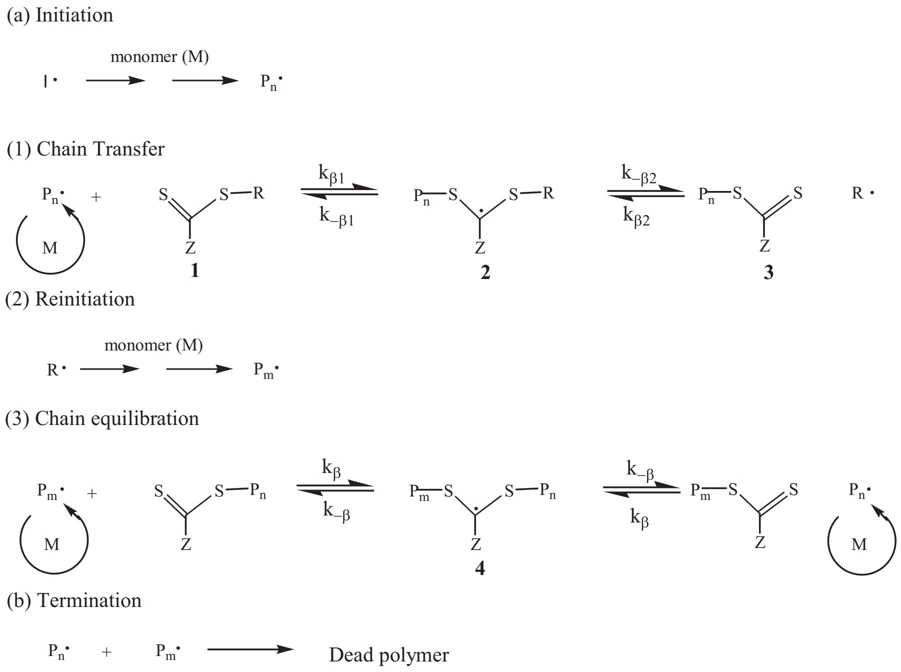

Figure 1.
Reactions in Reversible Addition Fragmentation Transfer (RAFT) polymerization.[24]

Acrylic acid (AA, Aldrich ≥ 99%) was distilled under reduced pressure in the presence of copper (copper fine powder extra pure, Merck) and stored in the dark at 7 °C before use. The monomers styrene, (STY, Aldrich 99+%) and n-butyl acrylate (BA, Aldrich 99+%) were purified by passing them through an inhibitor-removal column (Aldrich). The solvents propylene glycol (PG, BASF), 1,4-dioxane (Dx, Merck HPLC grade), were used as received. Water used during the BA experiments was Milli Q demineralized water. The water used for the styrene experiments was obtained from a Millipore Elix system. The initiator 4,4′-Azobis(4-cyanopentanoic

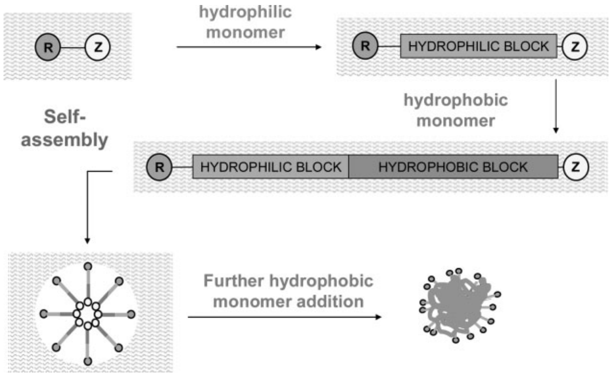

Figure 2.
Process concept used to create latex particles with amphipathic macro-RAFT agents, derived from Ferguson et al.[25]

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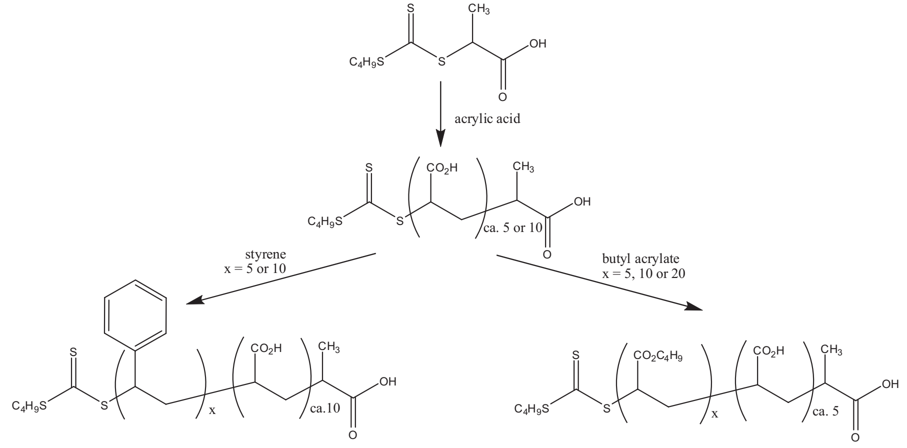

Figure 3.

Synthesis steps of amphipathic macro-RAFT agents that were subsequently used in controlled feed experiments growing × to a length of about 300 monomeric units.

acid) (V-501, Fluka > 98%) and sodium hydroxide (NaOH, Merck ≥ 98%) were used as received. Only high purity argon was used for deoxygenation.

Synthesis of Hydrophilic Macro-RAFT Agent

The RAFT agent and one molar equivalent NaOH, acrylic acid, initiator V-501 and Milli-Q demineralized water, propylene glycol or dioxane were added together in a round-bottom flask to obtain a 40% (w/w) solid content at complete conversion, see Table 1 for the molar ratios applied.

This mixture was capped with a rubber septum and degassed by purging with high purity argon while stirring with a magnetic stirrer bar. Subsequently the mixture was heated to the reaction temperature of 60 °C. The reaction mixture was kept at 60 °C for 2.5 hours while stirring. The resulting macro-RAFT agent was analyzed by Electrospray-MS.

Synthesis of Amphipathic Macro-RAFT Agent

Part of the previously formed macro-RAFT agent was converted into polymeric amphipathic macro-RAFT agents by growing a hydrophobic block of various lengths of either n-butyl acrylate or styrene onto it. The procedure for the synthesis is similar to that of the initial hydrophilic RAFT agent. Now the amphipathic RAFT agent with the hydrophilic block of acrylic acid is the starting RAFT agent. Once again all ingredients were added together in a round-bottom flask and degassed with high purity

Table 1.

Molar ratios related to the amount of the starting RAFT agent for the preparation of hydrophilic and amphipathic macro-RAFT agents.[a]

Macro-RAFT agents	RAFT	Monomer	Initiator V-501	Buffer NaOH	Solvent H_2O/Dx/PG	Solids contents full conversion
Hydrophilic	Dulux RAFT agent	5 or 10[b] (AA)	0.5	1 (only in H_2O)	H_2O/Dx/PG	0.4
Amphipathic	Hydrophilic macro-RAFT	5[c], 10[d] or 20 (STY or BA)	0.5		Dx/PG	0.4

[a] RAFT agent $25 \cdot 10^{-3}$–$75 \cdot 10^{-3}$ mol; [b] 10AA: reaction volume about 180 mL, initial amount of Dulux RAFT agent $75 \cdot 10^{-3}$ mol; [c] 5AA + 5STY: reaction volume about 200 mL, initial amount of hydrophilic macro-RAFT agent $75 \cdot 10^{-3}$ mol; [d] 10AA + 10STY: reaction volume about 250 mL, initial amount of hydrophilic macro-RAFT agent $50 \cdot 10^{-3}$ mol.

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argon while stirring. The reaction with n-butyl acrylate was started by heating up to 60 °C, which temperature was kept constant for 2.5 hours. The styrene experiments were performed at 70 °C in overnight runs. After the synthesis of styrene based macro-RAFT agents in 1,4-dioxane, the solvent was evaporated in a vacuum oven at 40 °C. The product was a dry yellow powder.

Controlled Feed RC-1e Experiments

A typical procedure based on styrene polymerization is described below, see Table 2.

The macro-RAFT agent was dissolved in 760 mL of an aqueous 0.05 M NaOH solution. This mixture was stirred for about 15 minutes, before it was added to the reaction vessel of the Mettler-Toledo RC-1e reaction calorimeter. The 1.8 dm^3 HP60 Hastelloy reaction vessel was equipped with a propeller stirrer. BA experiments were performed with Kalrez® perfluoroelastomer O-rings to prevent swelling of the O-rings with the monomer. The closed loop addition system consisted of Prominent pumps and Mettler Toledo balances connected to two Mettler Toledo RD10 control units.

After closing the reactor, the macro-RAFT solution was deoxygenated for the first time by introducing high purity argon to the reactor while stirring for four minutes. The pressure was released by venting for 1 minute while still keeping an argon overpressure. This five minute cycle was repeated three times, after which the reactor was heated to the reaction temperature of 80 °C. The stirring speed was set at 500 rpm. Subsequently the reaction mixture was calibrated using the calibration procedure integrated into the system. After calibration a 90 minute time interval was programmed to allow the mixture to return to the reaction temperature. Another four deoxygenation cycles were carried out, after which the reaction could establish a flat baseline. The initiator was dissolved in 100 mL of an aqueous 0.35 M NaOH solution in a flask equipped with a rubber septum. Before addition to the reaction mixture the initiator solution was deoxygenated by purging with high purity argon. A balloon filled with high purity argon was attached to the flask containing the initiator solution to keep an argon overpressure while the initiator solution was being pumped into the reactor.

The monomer was treated in the same way. The actual reaction stage was started by the addition of 50 mL of the initiator solution. During a 25 minutes interruption the system was allowed to come back to baseline. Subsequently the monomer feed was started by adding 15 grams of styrene over a period of four hours using the closed loop feeding setup. The heat effect of the monomer dosing was accounted for by estimating the heat necessary to heat up the monomer to reaction temperatures assuming a low constant temperature (25 °C) of

Table 2.
Experimental conditions for the controlled feed RC-1e experiments in the presence of macro-RAFT agents, respectively 5AA + 10BA and 10AA + 10STY, with a final RAFT/monomer ratio of 1:300.

Conditions	n-Butyl Acrylate		Styrene	
Temperature	60 °C		80 °C	
Agitation	Anchor @ 300 rpm		Propeller @ 500 rpm	
Initiator solution				
V-501	$2.0 \cdot 10^{-3}$ mol	0.56 g	$2.50 \cdot 10^{-3}$ mol	0.67 g
NaOH	$0.8 \cdot 10^{-2}$ mol	0.32 g	$1.75 \cdot 10^{-2}$ mol	0.70 g
H_2O	50 g		50 g	
Macro-RAFT solution				
H_2O	760 g		760 g	
NaOH	$1.6 \cdot 10^{-2}$ mol	0.64 g	$3.75 \cdot 10^{-2}$ mol	1.50 g
Macro-RAFT	$4.0 \cdot 10^{-3}$ mol	15.2 g PG mix	$5.00 \cdot 10^{-3}$ mol	8.67 g
Feeds				
Slow feed	15 g per 2 hours		12.43 g per 4 hours	
Fast feed	141 g per 4 hours		142.95 g per 5 hours	

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the monomer. Estimations were carried out with heat capacities reported in literature.[27] The styrene feed rate was increased to 142,95 g in the next five hours. After the completion of the monomer feed another two hours were used for the reaction to go to complete conversion and to return back to the baseline. The resulting latex was subjected to another calibration procedure and was afterwards cooled down to room temperature. The stirring speed was slowed down to 100 rpm.

Particle Size Distributions

Particle size distributions were determined by Transmission Electron Microscopy (TEM). Polystyrene TEM samples were prepared by drying latexes onto a carbon coated copper grid (200 mesh, Electron Microscopy Sciences). The solid content of the samples was in the range between 0.01% and 0.1%. TEM measurements were performed on a Philips CM 10, 12 and 120 Biofilter electron microscope, and a FEI Sphera and Titan electron microscope. The software package ImageJ[28] was used to analyse the TEM pictures.

Results and Discussion

Synthesis of Macro-RAFT Agents

A trithiocarbonate RAFT agent was used to prepare a macro-RAFT with, on average, blocks of five or ten acrylic acid units. This was first performed at similar conditions as described by Ferguson et al.[25]. However, much more RAFT agent was needed, because the reactions in the RC-1e are on a significantly larger scale. Firstly, the available RC-1e has a minimum load of about 0.65 dm^3 in the reactor, because with a lower volume the temperature probe and calibration heater are not submerged. Secondly, there is a minimum concentration of RAFT agent and monomer required for an an observable heat flow. This heat flow level was estimated from the noise level in a blank run to be approximately 0.5 Watt. For polymerizations under starved conditions this is equivalent to a feed of $7.7 \cdot 10^{-6}$ mol styrene per second (=2.89 g styrene per hour). In order to perform repeat experiments with macro-RAFT agents of the exact same composition, the first synthesis step had to be scaled up. An initial attempt was performed on a 0.10 dm^3 scale, in a 0.25 dm^3 round-bottom flask heated by an oil-bath and stirred magnetically. The increased reaction volume to surface ratio resulted in thermal runaway of the fast polymerization of acrylic acid. The formation of a high viscosity product mixture pointed to the formation of high molecular weight poly(acrylic acid). After this initial failure, the reaction was successfully performed with increased agitation by magnetic stirring and targeted at lower solid contents at complete conversion.

Electrospray mass spectrometry (ESI-MS) was carried out on the successfully synthesized initial hydrophilic macro-RAFT agent. The ESI-MS results confirmed the formation of the macro-RAFT agent with a relatively narrow molecular weight distribution, see Figure 4a. The product of the subsequent polymerisation with n-butyl acrylate was characterized in the same way, see Figure 4b.

These products are two examples for a range of successfully synthesized macro-RAFT agents. Although ESI-MS cannot be used to obtain a quantitative characterisation of the macro-RAFT agent, it does provide insight into the distribution of the different macro-RAFT molecules. It should be realized that a macro-RAFT agent identified as e.g 10AA + 10BA contains on the average 10 AA and 10 BA units. There is always a distribution of AA and BA or STY units.

Calorimetric Reactions

The synthesized macro-RAFT agents were used in controlled feed experiments in the RC-1e. These experiments all showed the same basic behaviour during the reaction, see Figure 5.

Figure 5 clearly demonstrates that reaction calorimetry is a proper tool to monitor the start of particle formation in *ab initio* emulsion polymerizations.

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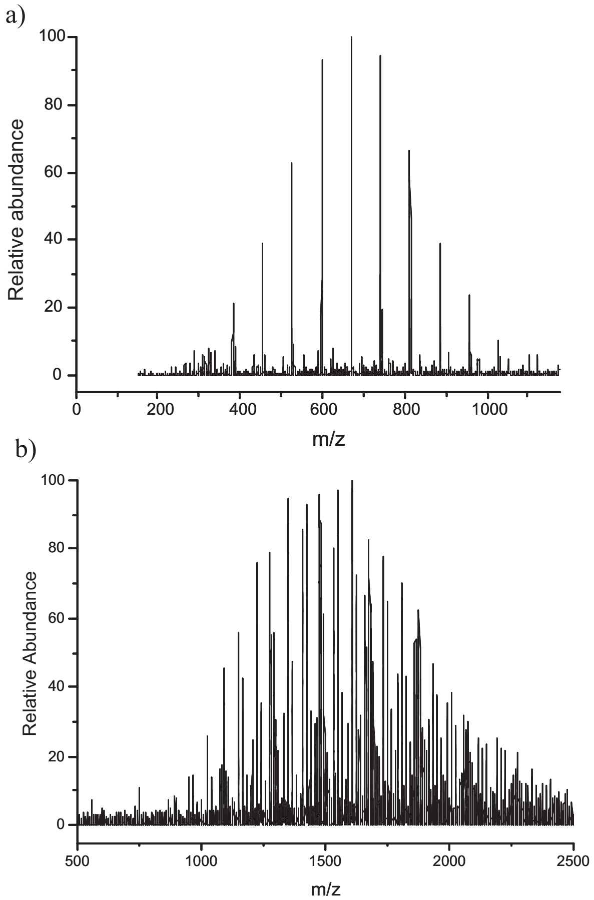

Figure 4.
Electrospray mass spectrum of macro-RAFT agent designed to contain five AA units (a) or five AA groups and 10 BA units (b).

Initially the macro-RAFT agent was dissolved in the aqueous phase, with a small amount of monomer present during the initial slow feed phase. Therefore a low polymerization heat flow was observed, if any. Subsequently the start of particle formation was clearly visible as a sharp increase of the heat flow. The free monomer in the system was rapidly converted into polymer. The reaction rate depends on the number of particles in the system, see Equation (1). Once all monomer added so far was converted, the polymerization continued under starved conditions. After two (BA) or four (styrene) hours the feed rate was increased. The rate of heat production promptly followed the feed rate and continued at the elevated level under starved conditions. Once the feed was stopped the heat flow immediately drops back to the baseline.

However, since the emulsion polymerization in the presence of amphipathic RAFT agents has to be performed under controlled feed conditions to prevent droplet polymerization, it is not possible to observe the duration of the particle formation period. The calorimetric data also revealed that even though very low monomer feed rates were initially used for all reactions, the monomer added before the start of particle formation is more than

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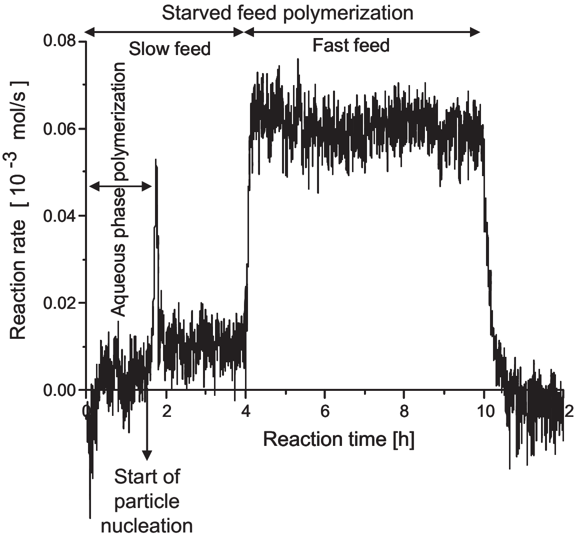

Figure 5.
Different stages in controlled feed RAFT-mediated emulsion polymerization of styrene.

can be dissolved in the aqueous phase. So, either there are some monomer droplets present or the monomer is distributed over the micelles already present.

Macro-RAFT Agents Compared

Macro-RAFT agents of various degrees of hydrophobicity have been synthesized and used in calorimetric experiments. For the n-butyl acrylate as well as for the styrene based experiments there was no difference in the behaviour after particle formation in the fast feed regime. During all reactions the rate of monomer consumption was equal to the feed rate. However, a clear trend was observed at the start of the reaction in the slow feed regime of the n-butyl acrylate experiments, see Figure 6a.

The more hydrophobic the initial RAFT agent was, the earlier the particle formation started. For the more hydrophobic macro-RAFT agents particle formation was followed by a rapid consumption of the monomer added up to that time, while the hydrophilic macro-RAFT took more than an hour to do so. This indicates fast particle formation for the most hydrophobic macro-RAFT agents which are probably already present as micelles at the start of the nucleation stage.

For the styrene polymerizations no such clear trend in the starting point of the particle formation was observed, see Figure 6b. This could possibly be due to inhibition.

However, once the feed rate is increased to the fast feed regime; the system with the more hydrophobic macro-RAFT agent (10AA + 10STY), adapts more rapidly to a new feed regime than the hydrophilic macro-RAFT agent (10AA). This points to more particles for the polymerization started with a macro-RAFT agent with 10AA + 10STY.

Table 3 summarizes the calorimetric observations for the different macro-RAFT agents.

Particle Size Distributions

Figure 7 shows the particle size distributions of the emulsion polymerizations started with the 10AA and 10AA + 10STY 10STY macro-RAFT agents as a function of the amount of styrene converted. The particle size distributions of the hydrophilic macro-RAFT (10AA) as well as the hydrophobic macro-RAFT (10AA + 10STY) 10STY) based latexes show a steadily increasing average particle size. However, the average particle size of the final product

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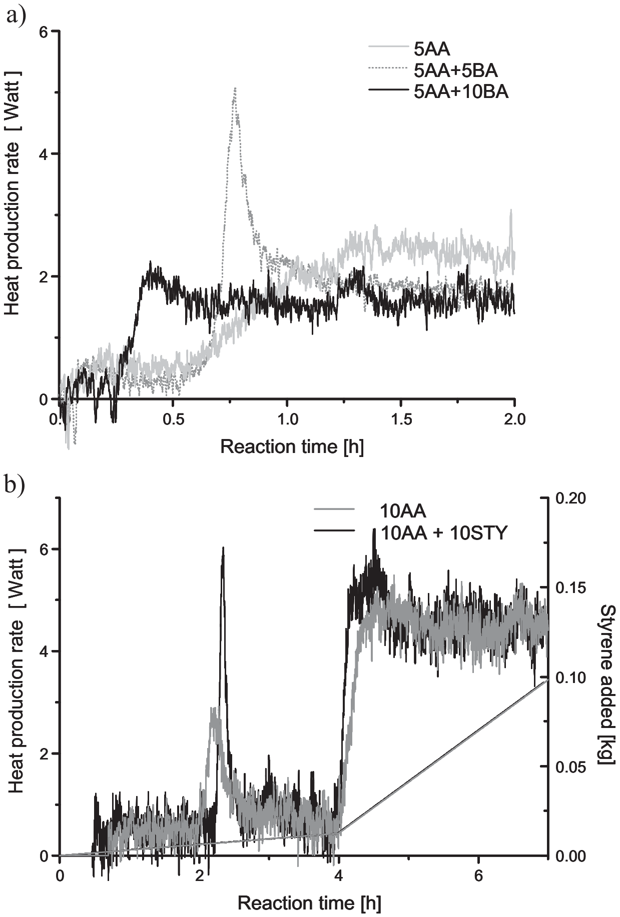

Figure 6.
a: Initial particle formation for different degrees of hydrophobicity of macro-RAFT agents in n-butyl acrylate controlled feed experiments. b: Initial particle formation for different degrees of hydrophobicity of macro-RAFT agents in styrene controlled feed experiments.

for the hydrophilic macro-RAFT mediated polymerization is much larger than for the polymerization using a hydrophobic macro-RAFT agent. Because the amount of styrene used is approximately the same for both macro-RAFT agents, the particle number for polymerizations with the hydrophobic RAFT agent is much higher than for the hydrophilic RAFT agent. During the reactions with the hydrophobic macro-RAFT agents probably micelles are formed which are nucleated. These particles

Table 3.
Start of particle formation and the time needed to reach steady monomer consumption for various macro-RAFT agents as measured with reaction calorimetry.

Monomer system	Macro-RAFT agent	Start particle formation [hours:minutes]	Steady monomer consumption after [hours:minutes]
BA	5AA	0:33	0:53
BA	5AA + 5BA	0:36	0:36
BA	5AA + 10BA	0:15	0:19
STY	10AA	1:56	0:52 (fast feed, Figure 6b)
STY	10AA + 10STY	2:13	0:21 (fast feed, Figure 6b)

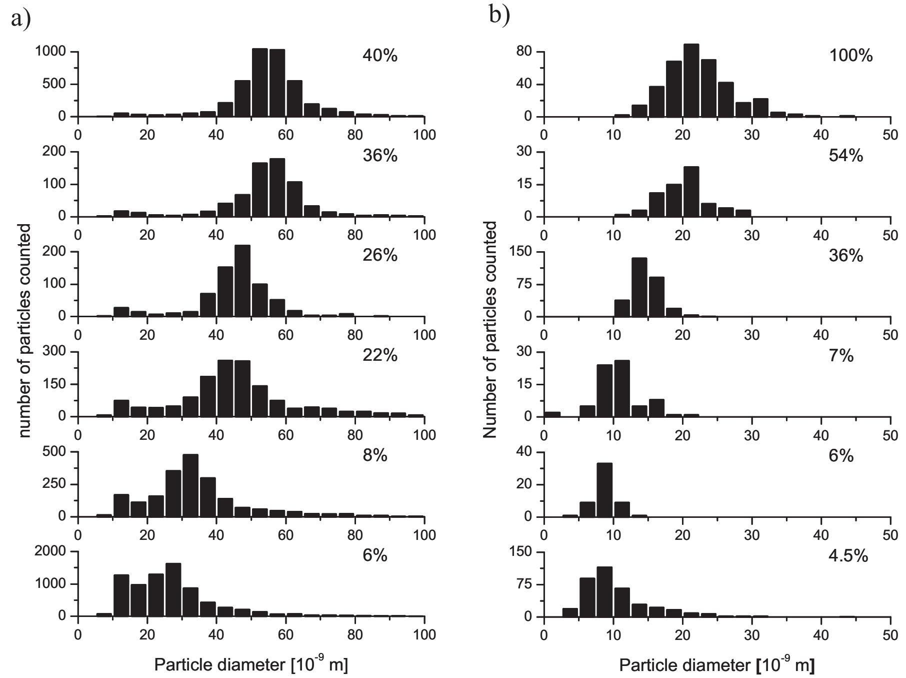

Figure 7.

Particle size distributions for macro-RAFT mediated emulsion polymerizations as a function of the fraction of the total amount of styrene supplied to the reaction mixture. a: hydrophilic macro-RAFT agent (10AA); b: hydrophobic macro-RAFT agent (10AA + 10STY).

formed grow steadily during the reaction. Note that nucleated micelles may take up diblock macro-RAFT molecules from micelles where polymerization has not yet taken place, see Ferguson et al.[25]. In polymerizations with a hydrophilic macro-RAFT agent, e.g. 10AA, micelle formation is negligible or even absent. Particles are formed by homogeneous nucleation. The particles grow and adsorb the remaining aqueous phase- or mobile surface active macro-RAFT agents, preventing additional micellar nucleation.

Conclusion

- Block copolymeric macro-RAFT agents with varying degrees of hydrophobicity have been successfully synthesized in a two step procedure.
- The macro-RAFT agents prepared are proper precursors for particle nucleation in n-butyl acrylate and styrene *ab initio* emulsion polymerization.
- For hydrophilic macro-RAFT agents homogeneous nucleation dominates. For hydrophobic macro-RAFT agents particles are mainly formed by micellar nucleation.
- With hydrophobic macro-RAFT agents more particles are formed than with hydrophilic macro-RAFT agents.
- Hydrophobic macro-RAFT agents are promising for producing latex products with a proper control of particle number and particle size distribution.
- Reaction calorimetry is an excellent and sensitive tool to monitor the course of *ab initio* emulsion polymerizations under starved feed conditions.

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