Mass Transfer in Miniemulsion Polymerisation

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Summary: The use of very hydrophobic monomers in heterogeneous polymerisations is restricted because of insufficient mass transfer as a result of limited aqueous phase diffusion. Experimental evidence for a mass transfer mechanism in miniemulsion polymerisation that is based on the direct interaction between droplets as well as between droplets and particles ('collisions') rather than monomer diffusion is presented. Mass transfer that results in the formation of a copolymer in the miniemulsion polymerisation of a mixture of lauryl methacrylate and 4-tert-butyl styrene, is almost non-existing when physical contact between individual droplets is prevented by a membrane. However, monomer transport by diffusion is observed in reference experiments with more hydrophilic monomers.

Keywords: *emulsion polymerisation, miniemulsion polymerisation, lauryl methacrylate, membranes, mass transfer*

Introduction

In the 40 years since it was first reported[1], miniemulsion polymerisation has developed towards a useful and very versatile method for the production of polymer in water dispersions. The characteristic feature that distinguishes miniemulsion polymerisation from conventional emulsion polymerisation is that particle formation takes place by entry of radical species into submicron monomer droplets rather than monomer-swollen micelles or via homogeneous nucleation. The most important requirements for droplet nucleation are the absence of surfactant micelles, the reduction of droplet sizes (*i.e.* a very large specific area per unit volume of the reaction mixture) to enable efficient radical capture and the colloidal stability of the formed droplets, at least during the time-frame needed for polymerisation. The key factor in miniemulsion polymerisation is the

formation and stabilisation of the monomer droplets. Formation of droplets requires shear, to be applied by, for instance, ultrasound, high-pressure homogenisers, static mixers or rotor-stator devices, *e.g.* ultra-turrax stirrers[2]. Once monomer droplets have been created, coalescence (i.e. fusion of two droplets) and Ostwald ripening (transfer of monomer from small to large droplets) reduce the number of droplets and change droplet diameters continuously. Successful retardation of this process can be established by a combination of a surfactant (against coalescence) and a so-called costabiliser. The costabiliser should possess very limited water solubility in order to create an osmotic pressure inside the monomer droplets that restricts Ostwald ripening. Historically, long-chain alkanes (*e.g.* hexadecane) have been used, but the use of monomer-soluble initiators[3,4], polymers[5,6] or reactive comonomers[7,8] has been reported to be successful as well.

One of the main advantages of miniemulsion polymerisation is the possibility to incorporate very hydrophobic monomers in the final latex particles, since the need for monomer transport across the aqueous phase is much less a prerequisite, given that the monomer is already at the locus of polymerisation. It is surprising, therefore, that the available literature on very hydrophobic monomers is scarce. Miniemulsion polymerisation studies towards hydrophobic monomers comprise lauryl methacrylate[9,10], isobornyl acrylate[11], isooctyl acrylate[12] and 4-tert-butyl styrene[10] The use of hydrophobic monomers as costabilizer is more widespread, for instance lauryl methacrylate[13], stearyl methacrylate[7,13] or octadecyl acrylate[5].

Besides offering a versatile route for the production very hydrophobic submicron polymer particles that are not accessible via conventional emulsion polymerisation, miniemulsion polymerisation of very hydrophobic monomers can also be of great academic interest. Since it restricts aqueous phase effects and allows the possibility to work in very diluted systems, it can give insight into mass transfer processes between individual droplets or particles.

A common misconception in miniemulsion polymerisation is that the compartmentalised nature of the monomer droplets automatically results in the absence of (significant) monomer transport between individual droplets. *Rodriguez et al*[14] have shown mathematically as well as experimentally that mass transfer takes place between submicron miniemulsion droplets in a miniemulsion consisting of either methyl methacrylate or styrene. However, the resistance of monomer transport in the membrane used in their compartmented diffusion cell was too high to allow for any monomer

transport within the time-frame of polymerisation. *Delgado et al*[15] modelled the diffusion of monomer in the miniemulsion copolymerisation of vinyl acetate and butyl acrylate and compared this to experimental results.

In this paper, we report investigations of monomer transfer in the miniemulsion (co)polymerisation of 4-tert-butyl styrene and lauryl methacrylate. The very hydrophobic nature of these monomers, resulting in water solubilities in the order of 10^{-5} mol/dm^3_w and 10^{-7} mol/dm^3_w respectively[16], substantially enlarges the resistance against mass transfer through the aqueous phase.

Experimental Part

Lauryl methacrylate (LMA, 96%), 4-tert-butyl styrene (TBS, 95%), methyl methacrylate (MMA, >99%) and n-butyl acrylate (BA, >99%), hexadecane (HD, 99%), sodium dodecyl sulfate (SDS, >99%) lauroyl peroxide (LPO, >97%), sodium persulfate (SP, >98%) and sodium carbonate (SC, >99%)) were all obtained from (Sigma-)Aldrich. Inhibitor-removal was done by passing the monomers over a column containing inhibitor remover (Sigma-Aldrich); all other chemicals were used as received. Deionized water (MilliQ standard) has been used throughout the experiments.

Monomer conversion was followed using a Perkin-Elmer Clarus 500 gas chromatograph, equipped with an Agilent Technologies HP-FFAP column. The conversion was measured against both an internal (HD) and external (toluene) standard.

Differential Scanning Calorimetry was performed using a TA-Instruments Q100 modulated differential scanning calorimeter. Polymer samples were precipitated in acetone (or ethanol in the case of PMMA/PBA) and washed with acetone (ethanol) at least 4 times. The washing liquid was kept aside after every washcycle and evaporated to check for any residue. The cleaned polymer was dried overnight at 80 °C. Three consecutive heating and cooling cycles (10°C/min, nitrogen atmosphere) were used for every polymer sample. Samples, typically 5-10 mg, were weighed into aluminium hermetic pans (TA-Instruments).

Particle and droplet sizes for the diffusion measurements were determined by photon correlation spectroscopy (PCS) using a Brookhaven Instruments BI-9000AT correlator with a Brookhaven BI-200SM goniometer set to a scattering angle of 90° and a 17 mW HeNe laser (632.8 nm wavelength). Samples were diluted with 3.3 g/L SDS solution to give a count rate of ~150 kcounts s^{-1} at the detector and, after temperature equilibration,

were subjected to 10 successive analyses of 1 min each. The vat temperature was held at ~25 °C (controlled to ±0.1 °C) and the exact vat temperature input when analysed the data using Brookhaven Particle Sizing Software v3.72 to obtain individual values of the particle diameter for each of the 10 measurements, the average of which was used to obtain the reported value (the standard deviation of which was typically ~2 nm). Blank measurements indicated that SDS micelles had no detectable influence on the results was. Reported diameters are z-averaged diameters (d_z), the width of the distribution is expressed by the so-called *poly*-value. For the calorimetric measurements, the d_z was determined on a Malvern Zetasizer Nano ZS. Latices were diluted with a 3.3g/L SDS solution. The Malvern Zetasizer has an internal filter which is automatically adjusted to give a count rate of ~400 kcounts s^{-1} Samples were thermostated at 20,0 °C (±0.1 °C). A single measurement consisted of 16 runs of 20 seconds each. The reported values are averaged over 3 measurements.

Miniemulsions were prepared according to the formulation given in Table 1. Water, SDS and (if applicable) SC were mixed together. When sodium persulfate was used, a small fraction of the water (usually 5-10 ml) was kept aside to dissolve the initiator. In a separate flask, the HD and LPO were dissolved in the monomer. Both the aqueous and monomer mixture were then transferred to a 400 ml beaker and stirred for at least 10 minutes using a magnetic stirrer bar. Subsequently, the mixture was ultrasonified for 30 minutes, using a Branson CV33 horn powered by a Sonics Vibracell VCX 750W at 65% output.

Table 1: Formulations used in the polymerisations (all amounts in grams)

	Monomer-phase initiated	*Aqueous-phase initiated*
Deionized water	200	200
Monomer	50	50
Hexadecane	2	2
Sodium Dodecyl Sulfate	1	1
Lauroylperoxide	0.795	-
Sodium Persulfate	-	0.476
Sodium Carbonate	-	0.212

To suppress polymerisation during ultrasonication, the beaker was immersed in an ice

bath. The resulting miniemulsion was checked for polymerisation by precipation of a few droplets into acetone, which showed no evidence of polymer formation.
In the case of miniemulsion copolymerisation or mixed miniemulsions, the monomer mass ratio was kept at 124.6 g LMA to 75.4 g TBS (51/49 mol/mol).
Diffusion measurements (with and without polymerisation) were carried out in an 800 ml stainless steel reactor (Figure 1), designed and built at the School of Materials in the University of Manchester. The reactor is divided into two equally-sized, symmetrical compartments using a Spectra Por 4 Regenerated Nitrocellulose membrane sheet (Spectrum Laboratories Inc.), clamped into a Teflon window frame. This membrane was soaked in deionized water for at least 30 minutes prior to reaction to remove glycerine traces and was replaced after every experiment. The measured membrane thickness was 38 μm, the reported molecular weight cut-off 12-14 kDalton. The exposed membrane area is approximately 40 cm^2.
Each compartment is stirred using a two-bladed impeller. The vessel is covered by a stainless steel lid which contains sample ports for the withdrawal of liquid samples and the supply of argon. The air tightness of the reactor was secured by a silicone material, fitted between the flanges of each compartment. Heating the reactor contents was done by immersing the reactor in a water bath, thermostated at 60°C. The time required to bring the reactants to reaction temperature, *i.e.*10 minutes, is comparable to jacketed vessels and glass reactors.
Each reactor compartment was charged with a miniemulsion, the amount being equivalent to the recipe used in Table 1. Both compartments were subsequently purged with

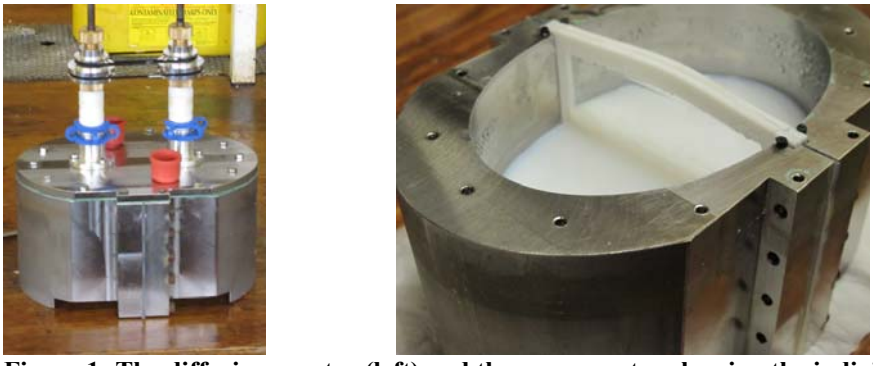

Figure 1: The diffusion reactor (left) and the open reactor showing the individual compartments separated by a membrane (right)

argon for at least 30 minutes, after which the reactor was pressurized by closing the argon exit. Polymerisations were started by immersing the reactor in the thermostated water

bath. In the case of persulfate initiation, this was followed by adding the initiator solution to each compartment. Equivolumetric samples were taken throughout the reaction from each compartment. Polymerisation of these samples was short stopped by addition of a few milligrams of hydroquinone. The reactor was kept under argon pressure during the reaction to prevent inhibition by oxygen.

A low monomer content (0.5% by volume) miniemulsion polymerisation was carried out in a 250 ml flanged round bottom glass vessel, equipped with a 4-neck glass lid, a reflux condenser and a 4-bladed impeller. 1.56 g of a standard LMA miniemulsion (see Table 1) and 0.94 g of a standard TBS miniemulsion were each diluted in 99 g of deionized water and subsequently added together, to obtain a 100-fold dilution (based on monomer/water ratio). Both miniemulsions contained LPO as the initiator.

All other miniemulsion polymerisations were carried out in a closed 1.6 L stainless steel Mettler-Toledo *RC1e* HP60 reaction calorimeter. The calorimetric profile was determined using the Mettler Toledo Icontrol 5.0 software and correlated to the final conversion measured by gas chromatography. Miniemulsions, made according to Table 1 but containing 4 times the indicated quantities, were charged to the reactor and subsequently degassed by bubbling argon through it. After this purging, the reactor was put under argon pressure and the reactor contents were heated to the reaction temperature (60°C). In the case of initiation by SP, the necessary amount (dissolved in 20 g of water) was added using a piston pump controlled by a balance. Throughout the reaction, the reactor was stirred at 250 rpm. The reactor internals acted as baffles.

Results and Discussion

In a first set of experiments, we compared the miniemulsion homopolymerization of LMA and TBS with the miniemulsion copolymerisation of these monomers, *i.e.* where the miniemulsion was prepared from a mixture of the two monomers. In a parallel run, we mixed separate LMA and TBS miniemulsions and allowed the mixture to react. We refer to the latter experiments as 'mixed miniemulsions□. Reactions were carried out with both SP (Figure 2A) and LPO as the initiator (Figure 2B). For a SP initiated system, it is apparent that the conversion-time history for the mixed miniemulsions is similar to the one for a miniemulsion copolymerisation, and does not show any resemblance to a

(combination of) the miniemulsion homopolymerisations. For the LPO initiated systems, we see again that the conversion-time history for the copolymerisation and the mixed miniemulsions are similar, albeit with a slight difference in the reaction rate caused by a difference in the number of particles.

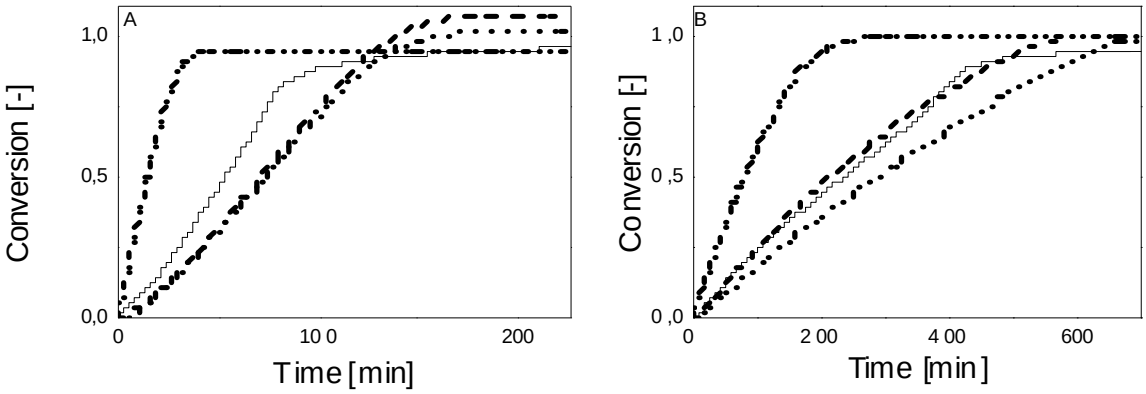

Figure 2: Conversion-time profiles for sodium persulfate (A) and lauroyl peroxide initiated miniemulsion polymerisations. (-••) LMA, (straight line) TBS, (- -) copolymerisation (••) mixed miniemulsions

Particle sizes of the final latices and glass transition temperatures (T_g) of the synthesized polymers are collected in Table 2. The measured glass transition temperatures indicate that the polymer particles created in the mixed miniemulsions polymerisation comprise copolymer particles rather than particles only containing poly-lauryl methacrylate or poly-tert-butyl styrene. Since the monomer droplets are the locus of polymerisation, the monomer composition in every droplet has to be the same and equal to the overall monomer composition. Dissolving of dried polymer in an (organic) solvent proved to be impossible, thus restricting the possibility for NMR or Gradient Polymer Elution Chromatography (GPEC) to obtain information about the copolymer composition. However, the fact that the conversion-time histories for the mixed miniemulsions and the copolymerisation do not differ at low conversion and the absence of transitions around the glass transition temperatures of the homopolymers demonstrate that the exchange of monomer between the droplets is rapid and is already accomplished before significant polymerisation occurs.

Note that these observations conflict with similar experiments published by *Ouzineb et al*. In a series of experiments, these authors showed by using DSC[8] and IR spectroscopy[17] that by polymerising a blend of miniemulsions containing either n-butyl methacrylate or styrene droplets, two homopolymers were obtained.

Table 2: Glass transition temperatures, final particle sizes and polydispersities for the sodium persulfate and lauroyl peroxide initiated calorimetric runs of the miniemulsion polymerisations of separately prepared miniemulsions of lauryl methacrylate and 4-tert butyl styrene.

		T_g [°C]	d_z [nm]	Poly [-]
Sodium persulfate initiated	*LMA (homopolymer)*	-46	127	0.01
	TBS (homopolymer)	128	109	0.03
	Copolymerisation	-1	133	0.01
	Mixed miniemulsions	3	143	0.07
Lauroyl peroxide initiated	*LMA (homopolymer)*	-46	168	0.10
	TBS (homopolymer)	119	151	0.06
	Copolymerisation	-1	155	0.09
	Mixed miniemulsion	-8	170	0.11

Although the water solubilities of these monomers are orders of magnitude larger than of TBS or LMA, no monomer transfer was observed. We have not been able to give a satisfying explanation for this yet, although the difference in the emulsifiers and costabilisers is worth mentioning. *Ouzineb et al* used a combination of an anionic and a neutral emulsifier (SDS and Triton X-405) together with the application of a reactive costabiliser. Our results, however, are based on hexadecane as the costabiliser and only an anionic emulsifier (SDS).

Mass transfer in (mini)emulsion systems is thought to occur mainly by diffusion. However, a second, parallel mass transfer mechanism based on particle-particle collision as a result of Brownian motion has received much less attention[18,19]. This mechanism has been postulated to be responsible for the transport of reagents with negligible water solubility such as inhibitor[20], long-chain alkanes[20], chain-transfer agents[21,22,23] or even monomers[11,12]. Since transfer of monomer by collision is a second-order process with respect to the number of droplets or particles, whereas transfer by diffusion is only a first-order process[18,24], working in a very dilute system would affect collision-based transport much more than diffusion-based transport.

For our miniemulsions, a 100-fold dilution was the the maximum possible dilution without losing droplet stability. The very low monomer amounts do not allow the use of SP as the initiator, since the ratio initiator to monomer ratio is then too high to overcome aqueous phase inhibition and termination. A too high cation concentration may also result in

compression of the charged bilayer. Hence, LPO was used as initiator for this experiment.
DSC analysis of the final polymer indicated one glass transition temperature at -1.5 °C which coincides with the glass transition of the copolymer obtained by mixing the undiluted miniemulsions and is only slightly higher than the glass transition temperature observed for the product of the miniemulsion copolymerisation. Although monitoring of the conversion by GC has not been done, since the low monomer concentrations do not allow for reliable measurement, it was apparent that the overall reaction rate was higher than the reaction rate observed for both the miniemulsion copolymerisation as well as for the mixed miniemulsions.
Because dilution of the miniemulsions did not clarify the mechanism of monomer transfer, spatial limitation of droplet-droplet interaction was chosen as a route to providing more insight into the mass transfer processes in (mini)emulsion polymerisations. Through separating two miniemulsion by a regenerated nitrocellulose membrane with molecular weight cut off in the order of 12-14 KDalton, we can distinguish between monomer transfer by collision and monomer transfer by diffusion. The small pores (pore sizes around 2 nm) form no barrier for single monomer molecules, but the pores are too small to permit the passage of monomer droplets across the membrane.
The water solubilities of MMA (0.15 M, 25°C)[25] and BA (0.015 M, 25°C)[26] are orders of magnitude higher than the aforementioned water solubilities of TBS and LMA. With a difference in homopolymer glass transition temperature of approximately 150 °C, MMA and BA serve as an excellent reference pair since monomer transport by diffusion is likely to occur.
In a first experiment, the permeability of the membrane for monomer was tested by equilibrating water, saturated with MMA, against deionized water at 60°C (Figure 3). Using Fick's law of diffusion (see equation 1), the molar flux through the membrane is given by

$$J_m = -D_{m,aq} \cdot \frac{\Delta C_m}{\Delta x} \qquad \text{eq 1}$$

in which $D_{m,aq}$ represents the diffusion coefficient, ΔC_m the monomer concentration difference between the retentate and the permeate side of the membrane and Δx the thickness of the membrane. a plot of the concentration against the logarithm of time should give a straight line, at least early in the experiment. Figure 3 shows that the membrane is

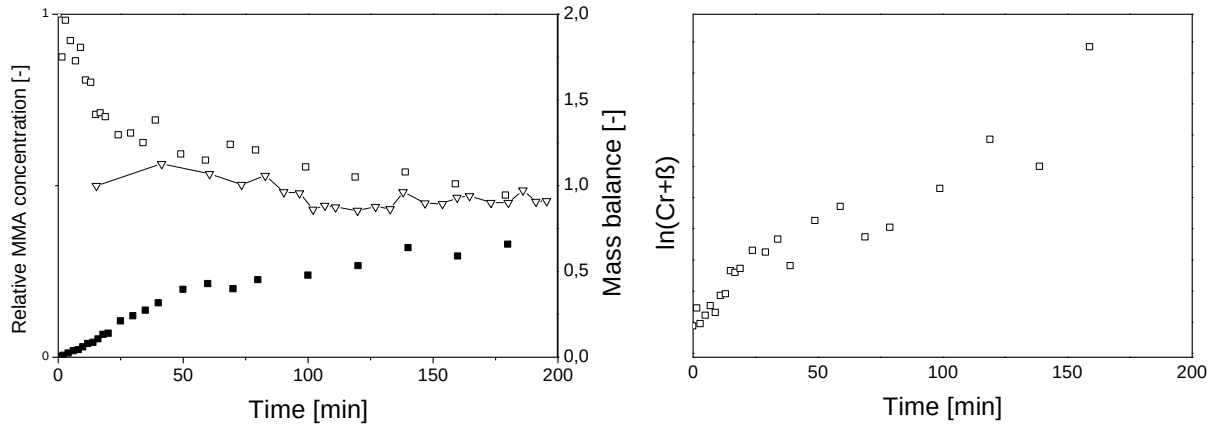

Figure 3: MMA diffusion across the membrane in a single phase system and . (□) MMA concentration in the MMA retentate, (■) MMA concentration in the permeate, (▽) total MMA detected in the reactor (mass balance)

readily permeable to MMA. By applying Equation 1 in a non-steady state mass balance, it can be shown that a plot of $\ln(C_r + \beta)$ against time should give a straight line, as can be seen in Figure 3. The retentate concentration is symbolised by C_r, whereas β is a constant, depending on the volume of permeate, retentate and the total amount of monomer. The time necessary for complete exchange shows that there is still a significant resistance against diffusion through the membrane. Note that the time constant for diffusion through the membrane is in the order of minutes/hours and not in the order of days[14]. The initial decrease in the mass balance is due to the absorption of a small fraction of the MMA by the rubber seals that prevent the reactor from leaking.

Permeability of the membrane for LMA and TBS has been tested in an 80/20 (wt/wt) acetone/water mixture. The use of acetone for this particular measurement was required due to the very low water solubilities of these monomers. The addition of water was necessary for membrane wetting. For LMA and TBS, membrane permeability was observed, although insufficient wetting of the membrane did not permit quantitative measurement.

To quantify monomer transfer in heterogeneous systems, we allowed 2 miniemulsion to equilibrate at 60°C. The equilibration of an MMA and a BA miniemulsion (Figure 4A) demonstrates that significant mass transfer is taking place within the time-scale for polymerisation. The diffusion rate of MMA is approximately 8 times higher than for BA, which is in agreement with the difference in water

solubility.

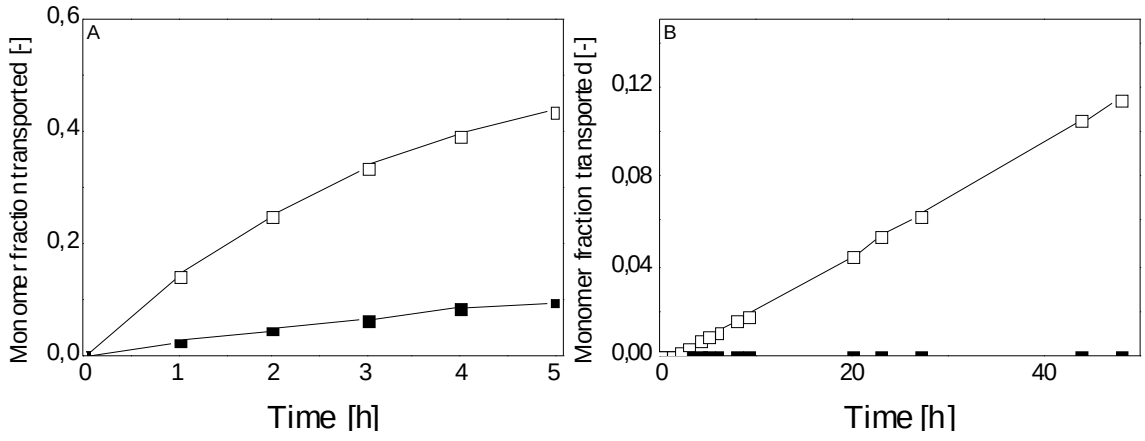

Figure 4: Monomer diffusion in heterogeneous systems for (A) (□) MMA, (■) BA and (B) (□) TBS, (■) LMA.

Note that the effect observed by *Rodriguez et al*[20] where more than 50% of the most water-soluble monomer is transported initially has not been observed, our measurement had to be terminated due to wearing of the seals.

Figure 4B shows the same measurement with an LMA and a TBS miniemulsion. Despite its very low water solubility, TBS does diffuse through the membrane, but this diffusion rate is too slow to have an influence during polymerisation. As expected, the extremely low water solubility of LMA restricts diffusion and not more than 0.05% of the total LMA amount has been found in the TBS rich compartment.

By adding initiator to the miniemulsions, we can monitor the influence of (the absence of) diffusion on the polymerisation. Figure 5 shows the compartmentalised miniemulsion polymerisations of LMA and TBS. For SP as the initiator (Figure 5 left), the conversion-time histories for both LMA and TBS are similar to those in Figure 2, which is in line with the short reaction times. By extending the reaction times (Figure 5 right), as a result of

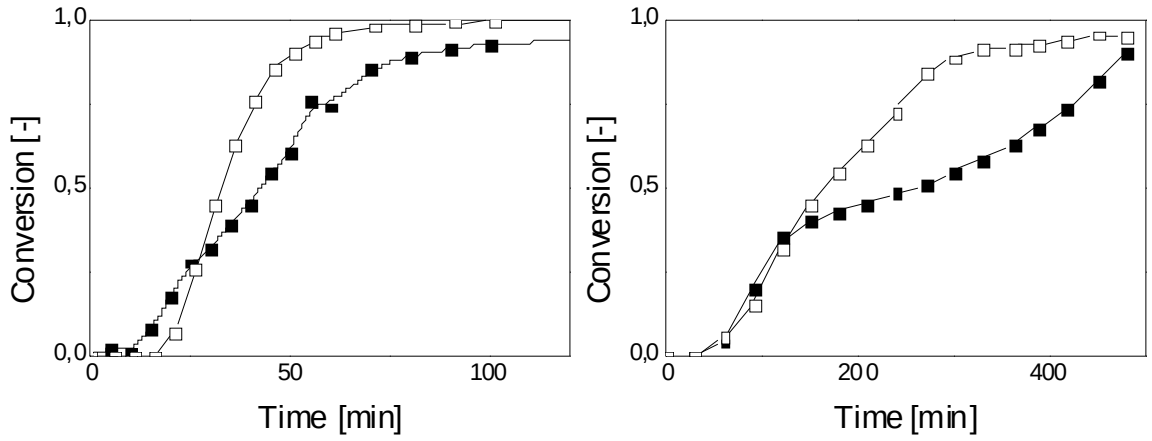

Figure 5: Conversion-time profiles for compartmentalised miniemulsion polymerisations of (■) LMA and (□) TBS for sodium persulfate (left) and lauroyl peroxide (right) initiation.

using LPO instead of SP, it becomes apparent that the rates of reaction are still similar to those observed for the miniemulsion homopolymerisations, indicating that the monomers are confined in their own compartments. Although according to Figure 4 not more than 0.5-1% of the total TBS amount is transported across the membrane and the measured TBS monomer fraction (g/g) in the LMA miniemulsion is around 0.1%, the influence on the rate of polymerisation is visible. The decrease in the polymerisation rate of LMA after approximately 50% conversion can be attributed to the reduction of the apparent propagation rate coefficient due to the TBS transferred. However, for LPO-initiated polymerisations, we also observed a decrease in the measured z-average particle diameters for the LMA particles and a strong increase in latex viscosity in both the TBS and LMA latex. The origin of this viscosity change is not clear yet. Note that addition of a small amount of inorganic salts (NaCl or Na_2CO_3) brought the viscosity back to normal values for latex systems with the solids contents used. Not surprisingly, the polymers in each latex had glass transition temperatures in agreement with those measured for the polymers produced in independent miniemulsion homopolymerisations (Table 3). Note that the DSC analysis of these diffusion measurements has been done on a different, but similar DSC than for the calorimetric runs, which accounts for the deviation in the measured glass transition temperatures. Moreover, the final particle sizes were different for each compartment (see Table 3), again indicating the presence of two different latices.

The polymers from the compartmented miniemulsion polymerisation of MMA and BA (see Table 3) had glass transition temperatures different from the corresponding homopolymers, indicating that mass transfer has taken place to some extent.

Again, to allow sufficient time for mass transfer, we included LPO as the initiator. Figure 6 shows the conversion-time histories and the instantaneous monomer composition during the reaction.

The relatively high rate of diffusion of MMA ensures an MMA fraction of 5-8% (mol/mol) in the BA minemulsion droplets. The BA fraction in the MMA droplets, however, does not exceed 1 mol%. Using the reactivity ratios r_{MMA} = 2.24 and r_{BA}=0.414[27], the fraction F_{MMA} incorporated in the polymer chains is expected to be around 0.15. Applying Fox' rule, the

measured glass transition temperature of -36 °C is close to the calculated value of -34 °C.

Table 3: Glass transition temperatures for the compartimented reactions.

	T_g [°C]	d_z [nm]	Poly [-]		T_g [°C]	d_z [nm]	Poly [-]
LMA homopolymer	-48	-	-	*BA homopolymer*	-48	-	
LMA (SP initiated)	-49	127	0.04	*BA rich polymer*	-36	128	0.12
LMA (LPO initiated)	-47	141	0.11	*MMA homopolymer*	125	-	
TBS homopolymer	152	-	-	*MMA rich polymer*	123	106	0.12
TBS (SP initiated)	153	100	0.04				
TBS (LPO initiated)	152	132	0.07				

Visual inspection of the reactor contents after polymerisation revealed that the liquid levels were differing by approximately 23 ml, the BA rich latex having the largest volume. Nevertheless, the solid content of this BA latex was 21.2% and therefore higher than expected from the original formulation, whereas the MMA latex had a lower solid content (15%) compared to the formulation. This difference in liquid level cannot solely be attributed to MMA diffusion. The higher monomer weight fraction in the BA miniemulsion, as a result of the MMA diffusion, creates an osmotic pressure between the two miniemulsions, resulting in a net transfer of water across the membrane.

The presented experimental results in this paper demonstrate that, in mixed miniemulsions, monomer redistribution among the monomer droplets takes place and is completed in the early stages of polymerisation. The experimental results also prove that neither monomer water solubility, nor the amount of monomer droplets is a determining factor in monomer mass transfer in miniemulsion polymerisation. When droplet-droplet interaction is prevented, by the introduction of a monomer-permeable membrane, it

becomes apparent that the exchange of monomer is almost completely restricted for very hydrophobic monomers, but still takes place for sparsely water-soluble monomers, albeit severely limited.

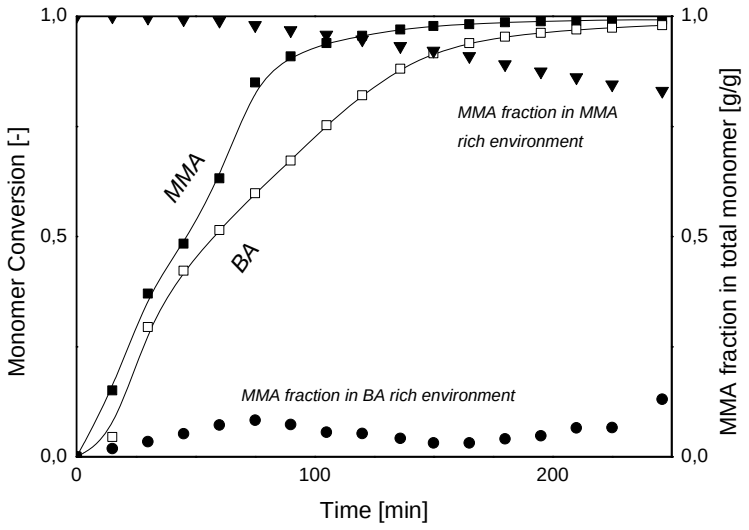

Figure 6: Conversion-time profiles for the compartimented miniemulsion polymerisations of (■)MMA and (□) BA and the MMA monomer fraction in (●) BA rich compartment and (▼) MMA rich compartment.

Summary and Conclusions

Despite the compartmentalised nature of a miniemulsion, mass transfer between individual droplets takes place. Mass transfer is a rapid process when two miniemulsions with different monomers are mixed together, the exchange of the monomer is accomplished at the very early stage of polymerisation, regardless the hydrophobicity of the monomer.

This rapid exchange observed in miniemulsions containing monomers such as lauryl methacrylate that are too hydrophobic to be used in conventional emulsion polymerisation, raises a question about whether this mass transfer is predominantly diffusion-based or collision-based. In the work described in this paper it was demonstrated that a 100-fold dilution in miniemulsion polymerisation, thereby increasing the diffusion distance and decreasing the collision probability, still resulted in rapid monomer transfer between the droplets.

When droplet-droplet interaction was restricted as a result of the use of a membrane, separating two miniemulsions, a difference in the mass transfer between sparsely water-soluble monomers such as methyl methacrylate and butyl acrylate and very hydrophobic

monomers such as lauryl methacrylate and 4-tert-butyl styrene was observed. While monomer transfer still takes place for sparsely water-soluble monomers, as observed in the formation of copolymers, it is restricted compared to mixed miniemulsions and monomer transfer was almost completely absent in the case of lauryl methacrylate and 4-tert-butyl styrene.

The results presented in this paper support the idea that mass transfer by collisions makes a major contribution in (mini)emulsion polymerisation.

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