Compartmentalisation in Miniemulsions: Exploration of Compartmentalisation and Some Interesting End-Uses

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Summary: Infrared spectroscopy and differential scanning calorimetry were used to demonstrate that miniemulsions of relatively hydrophobic monomers are compartmentalised during the reaction. Experiments with blends of miniemulsions of different composition revealed that no mass transfer takes place between droplets of different composition in the same reactor. In addition, it was shown that it is possible to make high solids content, low viscosity latexes with bimodal particle size and molecular weight distributions because of this property.

Keywords: bimodal molecular weight distribution; compartmentalisation; infrared spectroscopy; miniemulsion, polymerisation

Introduction

Most of the processes employed for the production of polymers (and most other materials) are evaluated in terms of basic economics: volume and cost of production, energy consumption, simplicity of execution and product quality. It is clear that these considerations are intimately related to the polymer characteristics and quality. Emulsion polymerization processes are therefore generally adjusted to tailor the properties of the final polymer, which will include the polymer composition, number of particles and particle size distribution, viscosity, molecular weight distribution, solids content, etc. The choice of the components, reactor configuration and process conditions will all have a great influence on the quality of the final polymer product. In the current paper, we will focus on how the means of generating particles can eventually be exploited to make products with different properties (see also Jovanovic et al.[1]).

Conventional macroemulsion polymerization has been widely used many years for the

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production of polymeric latexes that have numerous applications. The main components used in a conventional emulsion polymerization are water, surfactant, monomer and a water soluble initiator (other components can of course be included). In a typical synthesis, the latex is formed by agitating the first three components, which are then heated. Following this, the initiator is subsequently added, and free radicals are produced by thermal decomposition of the initiator. This allows us to generate particles either by creating micelles (micellar nucleation), or through the formation of particles via homogeneous or coagulative nucleation.[2] The final product is a stable colloidal suspension of submicron polymer particles in an aqueous media. Due to the partitioning of the components (polymerisation in one phase, generation of free radicals in another), high molecular weights and rapid reaction rates can be obtained simultaneously. The latex can be used directly (e.g. for adhesives or coatings), or the polymer can be extracted for other applications.

For the past several years, the production of latexes by polymerising miniemulsions has attracted a great deal of attention for many applications, essentially as an alternative to conventional emulsion polymerisation because of the way in which the particles are formed. In miniemulsions, the future loci of polymerisation are sub-micron monomer droplets, generated by combining a judiciously chosen stabilisation system with highly intensified mechanical mixing.[3,4,5,6] A miniemulsion is typically formed by intensely mixing an aqueous surfactant solution and an organic phase composed of monomer and a water-insoluble (hydrophobic) compound. Depending on the stabilisation system, and the intensity and uniformity of the mixing process, the oil droplets can range between 50 to 500 nm with a more or less narrow size distribution. These droplets are then usually polymerized with a water-soluble initiator as in classical emulsion. If the size of the droplets is sufficiently small, the resulting surface area allows the droplets to capture the oligomeric water-phase radicals and to become the main loci of polymerisation.[7] If they are properly stabilized, the number of particles at the end of the reaction will be the same as the number of droplets at the beginning. In an efficient miniemulsion, the vast majority of the droplets are nucleated, so that the ratio between the initial number of droplets and the final number of particles is close to one. This also opens up interesting applications in some processes where a good control of PSD is required. Ideally, the stage of particle nucleation with monomer transport through the aqueous phase is avoided (Interval I and II in the Smith-Ewart model of conventional emulsion polymerisation). This critical difference means that miniemulsions will behave differently from a kinetic point of view. Also, the properties obtainable with this type of system will be different, for instance the incorporation of hydrophobic components or the encapsulation of inorganic solids in the final polymer might be more efficient in miniemulsion processes.[8] The presence of this hydrophobic compound also means that monomer present in the droplets will not diffuse to the rest of the system for a good portion of the batch phase. In other words, the monomer is compartmentalised during the major part of a miniemulsion polymerisation. This point will be investigated in the present paper.

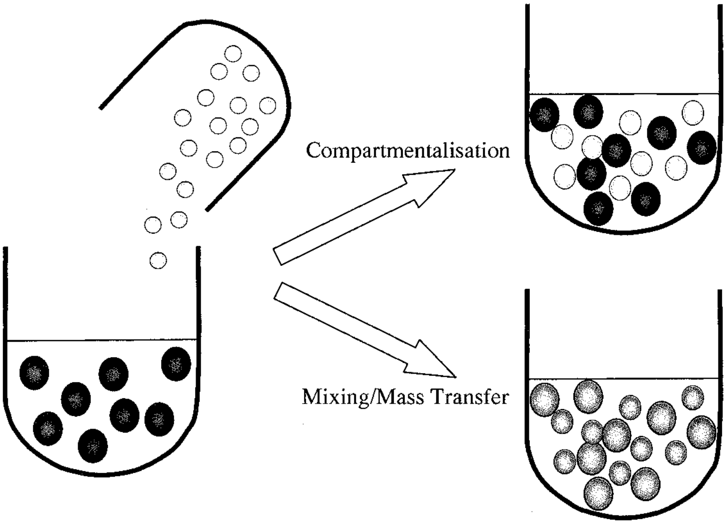

Figure 1. Schematic representation of alternatives when mixing 2 miniemulsions.

The issue that will be explored in this paper is shown schematically in Figure 1. If two separate populations of miniemulsion droplets are mixed, either the populations retain their identity throughout the reaction, or matter is exchanged to a more or less significant extent during the reaction. If mass transfer does not occur, this situation will be referred to as compartmentalisation.

If we consider a conventional macroemulsion, formed via micellar or homogeneous nucleation, it is clear that it is impossible to have compartmentalisation in the sense that we mean it here. This is due to the mechanism of formation and stabilisation of the final polymer product. In this case, the particles are formed either via micellar nucleation, or from some form of homogeneous or coagulative nucleation that takes place in the water phase. In either event, monomer must be transferred from an organic phase to the locus of polymerisation. This means that if more than one species is present in the reactor, they will all arrive at the reaction site after diffusing through the water phase, which in turn implies that it is almost impossible to segregate, or "compartmentalise" them in different parts of the reactor. On the other hand, if we take two populations of miniemulsions of monomer droplets with different compositions (either in terms of monomer or chain transfer agent), they can be formed separately and mixed together in the reactor. Since miniemulsions must contain a hydrophobic agent (often called a co-stabiliser or co-surfactant) to prevent Ostwald ripening (i.e. the transfer of monomer from one droplet to another), it is possible to eliminate a certain amount of mass transfer between droplets of different compositions during a significant part of the reaction. It is of course not possible to totally prevent monomer from dissolving in the aqueous phase to a certain extent, especially if one is using monomers such as methyl methacrylate (MMA) or vinyl acetate (VAc).

A legitimate question to ask is whether or not it is useful to exploit compartmentalisation, and if it might not be possible to simply polymerise different miniemulsions separately and then blend them to obtain the final product. In certain cases, this can be done easily. However, it has been shown that if one wishes to produce a high solid content (HSC) latex, it is necessary to polymerise populations of large and small particles together in a semi-batch reaction step.[9,10,11]. In this case, one can exploit the compartmentalised nature of minemulsions to make products that cannot be made with conventional macroemulsions.

Experimental procedures and techniques

Styrene, butyl methacrylate (BMA), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), Triton X-405 (70% in aqueous solution), and octadecyl acrylate (ODA) were obtained from Acros Organics and used as received. The chain transfer agent employed was dodecyl mercaptan (Acros Organics) and was used as received.

Emulsification of the mixture of water, monomer(s) and surfactant(s) was ensured by an ultrasonifier at 90% amplitude, which corresponds to a power input of 540 W. Miniemulsions were prepared by sonifying 500 mL batches of the different formulations for 4 minutes. More details on the experimental conditions and the reasons for choosing this stabilisation system can be found in Ouzineb et al.[5] Gravimetric measurements were performed on a limited number of the sonified samples to verify that no polymerization occurred during this step.

Polymerisations were carried out in a 2 litre glass reactor equipped with a reflux condenser, anchor stirrer and nitrogen inlet for runs not monitored by ATR-FTIR. The reaction temperature was controlled at 70°C by circulating water from a thermostatic bath in the reactor jacket. Dissolved oxygen was removed from the initial charge by bubbling nitrogen through it for half an hour before each run. At the end of the degassing period, the initiator was added in order to start the polymerisations. In the polymerisations carried out in a semi-continuous mode, the monomer was added at a constant rate under gravity flow, and the aqueous surfactant solution with a programmable syringe pump. Samples were withdrawn during the process and placed in vials containing hydroquinone to stop the reaction. Otherwise, the polymerisation procedure was the same, but the reactions were performed in a 1.5L LabMax™ automated reactor system equipped with a ReactIR™ 1000 ATR-FTIR probe (ASI Applied Systems, Inc., Mettler-Toledo).[12,13] In this case, the ATR-FTIR probe was inserted through a port in the reactor head. The position of the probe was approximately 2mm from the stirrer. For an optimal signal to noise ratio, the number of scans and resolution were set to 128 and 16 cm^{-1}, respectively. In all reactions, a background spectrum and the reaction spectra were collected using these conditions. During the course of the reaction, spectra were collected every 2 minutes.

Overall conversions were determined gravimetrically. The glass transition temperature measurements were performed using a Setaram DSC 131. Dynamic laser light scattering or quasi elastic light scattering (QELS) (Autosizer 4700, Malvern Instruments Ltd) was used to determine particle size and distribution. Only the repeated runs were analyzed using QELS. Measurements were recorded at a 90° angle and an average of ten measurements was recorded. The CONTIN mode in the Malvern PCS software was used for the analysis of the results. A Waters gel permeation chromatograph (GPC) was used for the determination of the molecular weight distribution of the latexes. Three Waters Ultrastyragel columns (10^3, 10^4 and 10^6 Å) were used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 mL/min at 38°C. Polystyrene standards (SHODEX) with molecular weights between 1.3×10^3 to 3.15×10^6 g mol^{-1} were used for calibration. Standards and samples were prepared in THF and filtered prior to injection through 0.45 μm filters to remove high molecular weight gel, if present. The injection volume was 200 μL. Millennium32™ software (Waters) was used for data acquisition and analysis.

Results and Discussion

In an initial step, the miniemulsions shown in Table 1 were monitored using the ATR-FTIR probe. Runs 1 and 2 are homopolymerisations that were conducted in separate reactors, Run 3 is an experiment where unpolymerised latexes identical to those of Runs 1 and 2 were prepared separately and reacted together after being blended in the reactor. Run 4 was a copolymerisation where the monomers were mixed together before preparation of the miniemulsion.

Table 1. Experimental conditions.

	Styrene (% wt/total)	BMA (% wt/total)	ODA (% wt/monomer)	SDS (× CMC)*	Triton (× CMC)$^+$	APS (% wt/total)
Run 1	38	-	2	0.5	8	0.03
Run 2	-	38	2	0.5	8	0.03
Run 3	19	19	2	0.5	8	0.03
Run 4	19	19	2	0.5	8	0.03

* CMC of SDS = 1.6 g/l at 25°C (preparation temperature) [14]
+ CMC of Triton = 2.0 g/l at 25°C[15]

The results of the IR analysis are shown in Figure 2 for the homopolymerisations and in Figure 3 for the polymerisation of the blend and the copolymerisation. Absorbance bands such as those at 1452 cm^{-1} representing the ring semicircle stretching for PS, or at 2880 cm^{-1} for the $-CH_3$ symmetric stretching of PBMA were found to be suitable to follow the appearance of the homopolymers as they are absent in the zero conversion spectra.

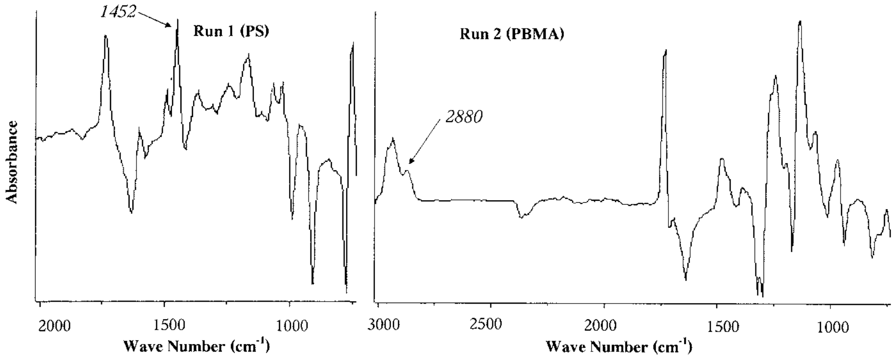

Figure 2. IR spectra of Runs 1 and 2.

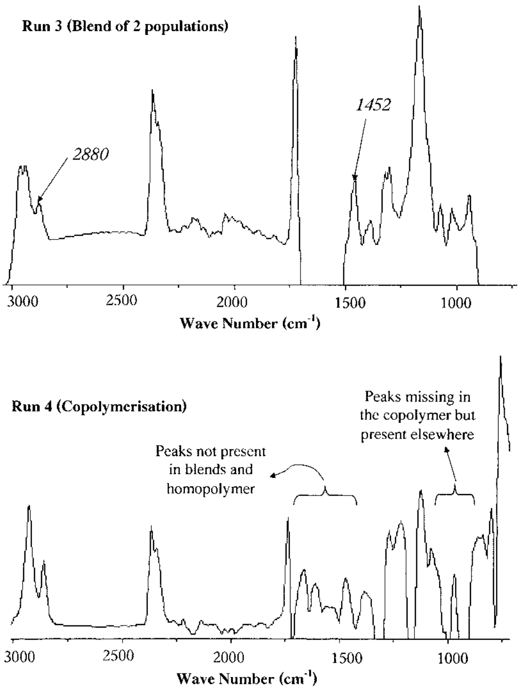

Figure 3. IR spectra of Runs 3 and 4.

It can be seen that there is a significant difference between the spectra in Figure 3, which means that the product of a blend of miniemulsions (Run 3) is chemically very different from the copolymer produced in Run 4. This is true for the entire set of spectra collected during the experiment. In the event that mass transfer occurred between the different particles in Run 3, peaks corresponding to the formation of a copolymer species should be evident. In this case, the copolymer peak would not necessarily be found at exactly the same position as in Run 4 given that we cannot guarantee that the composition in the particles in Run 3 would be the same as in Run 4. Nevertheless, as can be seen from these figures, none of the peaks unique to the copolymer (i.e. in the copolymer spectrum and not in the homopolymer spectra) were formed in Run 3. In addition, the spectrum for the final latex from Run 3 is very close to being the sum of the spectra of the two homopolymers shown in Figure 2. These results suggest that, in the case of these two hydrophobic monomers, no discernable mass transfer occurred between the two particle populations, and that we can consider the monomer in the particles to be compartmentalised in the original droplets.

Nevertheless, the possibility that a small amount of mass transfer occurred once the concentration of monomer in the particles dropped below the saturation value of conventional macroemulsions since at this point the hydrophobe is consumed by the polymerisation and there is essentially little difference between the mini- and macroemulsions at this point (from a thermodynamic point of view). These results support the argument put forth by Ouzineb et al.[5], who used DSC analysis to demonstrate this same effect.

Since miniemulsions of styrene and butyl methacrylate are compartmentalised in terms of the mass transfer between the droplets, it is possible to exploit this property to create latexes with high solids content and chemical properties different from those obtainable in macroemulsions. As outlined by Boutti et al.[11], the production of a high solids content latex (high solids meaning over 60% volume fraction of the organic phase) can take the form of a 4 step process:

1. The generation of a well-defined seed (number and size of particles).
2. The concentration of this seed and growth of seed particles.

3. The injection of a second population of smaller particles.
4. The concentration of the latex and the competitive growth of the two particle populations.

Note of course that other processes are possible.[9] We will concentrate on this particular route here.

Table 2. Recipe used for the batch miniemulsion polymerization of seed used in 5.

Recipe				
Sty (% wt/total)	**SMA** (% wt/Sty)	**SDS** (x CMC)	**Triton** (x CMC)	**KPS** (%wt/total)
39	0.50	0.15	4.5	0.13
Characterization of dispersions				
d_m nm	**$PI_{initiale}$**	**$d_{p\,final}$ nm**	**PI_{final}**	**$N_{m,i}/N_{p,f}$**
265	0.16	275	0.06	1.2

d_m = Diameter of monomer droplets, PI = polydispersity index, $d_{p,final}$ = final particle diameter, $N_{m,I}$ and $N_{p,f}$ are number of monomer droplets and polymer particles respectively.

Table 3. Recipe used for the second seed used in Run 5.

Recipe					
BMA (% wt/total)	**SMA** (% wt/BMA)	**SDS** (x CMC)	**Triton** (x CMC)	**KPS** (%wt/total)	**nDDM** (%wt total)
53 %	2%	0.15	4.5	0.13	2

Run 5 is a 4-step process as described above. The seed was made as shown in Table 2. 114 g of this seed were then concentrated by adding 640 g of styrene (neat) at a constant flow rate for 240 minutes to yield a concentrated seed latex (corresponding to Step 2 in the list above) with the PSD shown in Figure 4. Once the solids content was equal to 63 wt%, the styrene feed was interrupted for 30 min to reach complete conversion of residual monomer. A sample was withdrawn to measure the viscosity and PSD at this stage of the reaction (i.e. a latex at 63 wt% solids content with a monomodal PSD). Step 3 was begun with the addition of 151 g of a BMA miniemulsion (56% solids, d_m = 152 nm, d_m = Diameter of monomer droplets, PI = polydispersity index, $d_{p,final}$ = final particle diameter, $N_{m,I}$ and $N_{p,f}$ are number of monomer droplets and polymer particles respectively.

Table 3), which was added over the course of a few minutes, following which styrene was once again added for 40 minutes. The final latex was obtained after a finishing period (batch). The PSD of the final latex is given in Figure 4, and the molecular weight distribution (MWD) of the intermediate and final latexes for Run 5 are given in Figure 5.

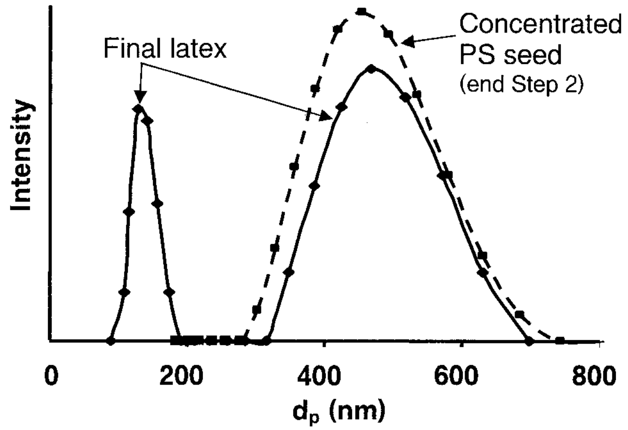

Figure 4. PSD of the latex in Run 5 at the end of the second step (concentrated seed, ----), and of the final latex (——).

At the end of the seed concentration step, the ratio of the number of droplets in the initial styrene miniemulsion to the number of particles was 1.01, with an average d_p = 460nm. At this point the viscosity was 690 mPa·s at a shear rate of 20 s^{-1} and a solids content of 63% by weight. The final latex contained the bimodal PSD shown in Figure 4, and the viscosity was 56 mPa·s (same shear) for a solids content of 63% (w/w). The latex was centrifuged, and it was found that the supernatant phase contained only small particles with a diameter of 147 nm (very close to the d_m of the original BMA miniemulsion), and that the precipitate contained a bimodal distribution with small particles of d_p = 149 nm and large particles with d_p = 468 nm.

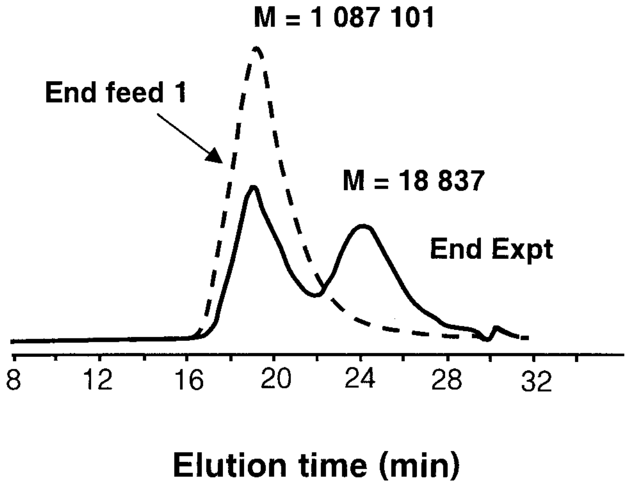

Figure 5. MWD of the latex in Run 5 at the end of the second step (concentrated seed, ----), and of the final latex (——).

These results all support the idea that both the monomer and the chain transfer agent remain compartmentalised in the original particle populations during the reaction. In addition, it should be noted that the experimental protocol described above allowed for styrene monomer to be fed in during Step 4 (concentration of latex with 2 populations) while the BMA in the second seed was in the course of polymerising. It is very interesting to note that the styrene did not enter the BMA droplets during the 40 minute feed period, but rather only entered the PS particles. This is supported by two pieces of evidence. First of all, the growth of the PS particles (assumed to be the large population in the precipitate phase of the centrifuged latex) corresponds closely to the amount of styrene monomer added during Step 4. Secondly, the thermal analysis of the final latex (shown in Figure 6) reveals the presence of two rather well-defined glass transition zones that correspond to what one would expect to find for the two homopolymers and there is no evidence of a T_g corresponding to a copolymer of styrene and BMA.

This observation can be explained by the compartmentalisation of the system. The PS particles were essentially monomer-free particles, and for all intents and purposes could be treated as macroemulsion particles at the end of a run. They can therefore easily absorb any monomer added to the reactor. On the other hand, the population of BMA particles was composed of particles that are "super-saturated" with respect to monomer levels that one could expect to find in a macroemulsion because of the presence of the hydrophobe. Thus, not only is the BMA stopped from leaking out to the PS particles, but no monomer can enter into these particles until they begin to approach the saturation levels common for macroemulsions (which did not happen here as the styrene feed lasted for only 40 minutes, and the conversion of BMA was estimated to be approximately 30% at this point).

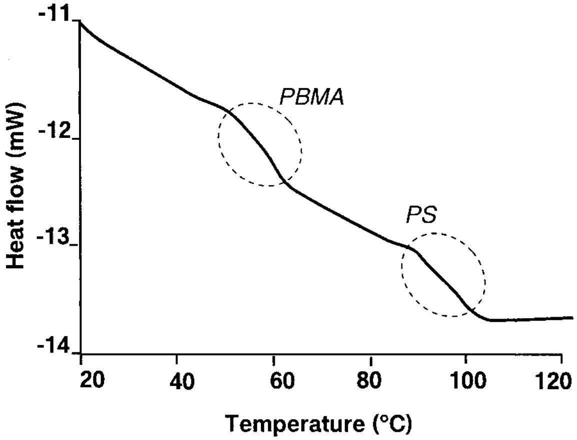

Figure 6. Calorimetric evaluation of the glass transition temperature of the latex in Run 5. Two clear T_g's are seen, with nothing that really corresponds to the formation of a copolymer.

Conclusions

The results presented in this article support the idea that miniemulsions can be thought of as (at least partially) compartmentalised systems in terms of monomer and chain transfer agent. Monitoring of miniemulsion polymerisation with ATR-FTIR spectroscopy allowed us to identify characteristic peaks for the different species involved (styrene, PS, BMS, PBMA, and the copolymer of styrene and BMA). The peak assignments clearly revealed that the polymer obtained with the blending of the two miniemulsions prepared separately (styrene miniemulsion

+ BMA miniemulsion) but polymerised together had the same characteristic peaks as the homopolymers. Analysis by both infrared spectroscopy and by differential scanning calorimetry show that populations of miniemulsions with different monomer compositions can coexist and polymerise in the same reactor with no mass transfer taking place between them (on a detectable level). This is also true of chain transfer agent, and, under certain conditions, monomer feeds added semi-batchwise to a mixture of populations of different composition.

It is believed that this property of miniemulsions is not simply a scientific curiosity, but rather that it can be exploited to tailor the properties of latex properties such as adhesives where low and high molecular weight molecules are needed to control both tack and peel resistance simultaneously. More work is needed in this area, but the possibilities seem very realistic.

Acknowledgements

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