Continuous Production of Miniemulsions Using In-Line SMX Elements

Ula El-Jaby
Dept. of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

CNRS-LCPP/CPE-LYON, BP 2007, Université Claude Bernard Lyon 1, Villeurbanne, 69616, France

Michael Cunningham
Dept. of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

Timothy F. L. McKenna
Dept. of Chemical Engineering, Queen's University, Kingston, Ontario, Canada

CNRS-LCPP/CPE-LYON, BP 2007, Université Claude Bernard Lyon 1, Villeurbanne, 69616, France

DOI 10.1002/aic.12365

The preparation and stabilization of miniemulsion systems using SMX static mixers (in line with a pump and reservoir tank) and in situ generated surfactants is presented. Neutralization of a water-soluble base with an oil-soluble long chain acid, generating a in situ surfactant at the interface, results in rapid stabilization and emulsification compared to preformed surfactant that must diffuse to, then adsorb on the droplets. As the flow rates (50–75 g/s) and number of mixing elements (7–21 SMX mixers) in series increase, the emulsification time reduces by ~30-folds (14 vs. 0.5 min). The reduction in the emulsification time required to produce a stable emulsion at 75 g/s and 21 mixing elements more than compensated for the higher pressure in the emulsification loop, consuming five times less energy than what would be consumed when working at 50 g/s and 7 SMX elements. Subsequently, with the rapid emulsification step, it was possible to test the feasibility of a continuous process for direct emulsification followed by polymerization. Comparing this process with a batch process, similar results for the number of particles/number of droplets ratio and conversion were obtained, but the continuous process was accomplished in a single step. *AIChE J,* 57: 1585–1594, 2011
Keywords: miniemulsion, SMX elements, continuous, in-line, in situ, polymerization

Introduction

Miniemulsion polymerization is a heterophase polymerization technique offering unique advantages over traditional conventional emulsion and suspension polymerization processes. Miniemulsions have been extensively researched within the academic community and have recently sparked an increasing amount of industrial attention due to their ability to encapsulate hydrophobic materials. Miniemulsions are typically composed of stabilized oil in water droplets with diameters on the order of 50–500 nm. A defining feature of miniemulsions is that in an ideal situation, each droplet behaves as an isolated batch reactor and therefore the number of particles (N_P) at the end of the polymerization matches the number of droplets (N_D) initially present after emulsification ($N_P/N_D = 1$).

Often a requirement for a successful polymerization is a narrow droplet distribution that has been stabilized against

---

Correspondence concerning this article should be addressed to T. F. L. McKenna at tim.mckenna@chee.queensu.ca.

coalescence and Ostwald ripening using a surfactant and costabilizer, respectively. The costabilizer is typically a low molecular weight compound that is highly insoluble in water and highly soluble in the monomer phase. Incorporating the costabilizer in the dispersed phase creates an osmotic pressure gradient that significantly reduces the amount of monomer transfer from smaller to larger droplets via Ostwald ripening.[1] The surfactant molecules play different roles during both the stabilization and emulsification processes. During emulsification, surfactant (electrostatic and/or steric) molecules are transported to newly generated interface and adsorb onto the newly formed oil-water surfaces. Once adsorbed, they lower the interfacial tension, facilitating subsequent droplet breakage and stabilise the newly exposed surface of droplets to varying degrees against coalescence. It has been shown that adsorption of the surfactant is the rate controlling step, with respect to droplet breakage, in the droplet formation and stabilization process.[2] A certain amount of droplet coalescence during emulsification is unavoidable, as the stability is dependent on the rate of surfactant transport within the system and adsorption onto newly formed droplet surfaces. However, after repeated breakage/coalescence cycles, equilibrium between droplet breakage and coalescence is established and the system reaches a minimum (equilibrium) droplet size. In a recent publication we reported that the time to reach equilibrium can be significantly shortened by using a surfactant generated in situ prepared by neutralising an oil-soluble carboxylic acid with a water-soluble base.[3]

It appears that the rapid generation of oil-soluble surfactant at the interface reduces the amount of coalescence during breakage cycles and the amount of secondary nucleation during polymerization. A previous study using a rotor-stator mixer to emulsify a mixture of water and oil (methylmethacrylate and butyl acrylate (BA) in a 1:1 weight ratio with a total organic phase weight fraction of 0.44) showed that 170 nm sized droplets could be prepared after 20 minutes of emulsification using in situ generated potassium stearate (KSA).[3] This is compared to an emulsification time of 40 minutes for droplets prepared with the preformed counterpart (*p*KSA) and 60 minutes when using commercially available sodium dodecylbenzene sulphonate (SDBS).[3] The reduction in emulsion time was partially attributed to the elimination of the relatively slow adsorption step. It therefore appears possible to obtain further improvement in the production of miniemulsions by developing more effective homogenization processes.

Homogenization devices are rarely investigated in theoretical miniemulsion studies but play a fundamental role in determining the viability of a commercial process. A range of devices has been widely used within the academic community, with ultrasonication (US) being the most popular due to its simplicity and ease of operation. However, US has significant drawbacks preventing commercialization, such as the need for constant recirculation of the entire reaction volume near the probe tip using a standard magnetic stir bar. The inconsistency usually results in wider droplet size distributions and/or undetectable very fine satellite droplets (due to excessive shearing); a problem that will be amplified if scaled to larger volumes. More importantly, the heat generated due to the high shear ($>10^6$ s^{-1}) needs to be quickly removed to prevent degradation or premature polymerization.[4] Another common bench scale device, which is widely used in the dairy industry, is the high pressure homogenizer. The coarse emulsion requires several cycles within the high shearing zone, at very high pressure ratings (5–50 MPa), before reaching a minimum droplet size.[5] Emulsification time can be reduced if the pre-emulsified mixture is sonicated, which reduces the droplets to the micron size range. Similarly, rotor-stators (RS) require constant recirculation in the high shearing zones located between the rotating blades and the stationary stator.[6] Determining appropriate dimensions and operating parameters is based on trial and error and even then mixing profiles cannot be determined with absolute certainty as the fluid flow through the mixing head is a very complex and dynamic process, typically resulting in wider droplet size distributions.

On the other hand, we have shown that static (or motionless) mixers (SM) installed in a recirculation loop in-line with a pump generates droplets comparable in size to those generated with US or RS.[7,8] Additionally, SMs generate narrower droplet size distributions and impose less shear in comparison to US and RS. SM, which fit flush within tubes or pipes, create plug flow conditions and induce flow in the radial direction. Immiscible phases entering the SM are split into layers that are then reoriented, folded, and redistributed. The process is repeated at every additional mixer. Elongational stresses are the major contributors to droplet size reductions within the laminar region and inertial forces dominate as the flow progresses into transitional and turbulent regimes. SMs can vary in size depending on the application and require power supplied by a pump to offset the pressure drop across the elements. A number of SM are commercially available, differing geometrically but operating in a relatively similar fashion.

Zalc et al. ran numerical simulations to assess the mixing performance of SMX (Sulzer ChemTech) mixers and compared them to experimental results.[9] They examined the evolution of the mixing patterns of flow within the laminar regime. Computational simulations, identifying variations in pressure, velocity and shear rates along the length of the element for flow in the laminar regime has also been reported.[10] Rauline et al. examined tracer distributions and compared numerical to experimental mixing efficiencies of SMX and Kenics (helical elements by Chemineer) mixers.[11] Separately, Heniche et al. compared SMX to KMX (curved crossbars by Chemineer) mixers.[12] They examined the effects of parameters such as pressure drops, intensity of segregation, stretching, shear rates and residence times for a number of elements. It was found that SMX elements were superior in mixing performance and generated droplets 2–3 times faster than Kenics mixers. However, KMX elements were slightly more efficient than SMX elements due to their curved blades, inducing additional mixing at a cost of higher pressure drop. SMX elements were used throughout our investigation due to their performance and efficiency in terms of shear rate.[13] Each SMX element consists of X-shaped cross bars aligned at 45° to the axis of the pipe, with each additional element angled at 90° relative to the previous element (Figure 1).

The majority of the research published to-date concerning SMX elements has focused on computationally modeling the mixing patterns. Experimental studies have investigated the preparation of millimeter and micron-sized droplets but very

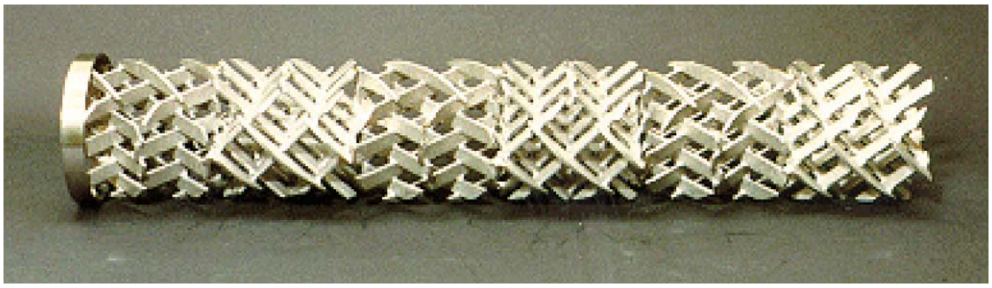

Figure 1. SMX mixers (Image courtesy of Sulzer Chemtech).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

little work has been done with droplets in the nanometer size range.[14–19] Ouzineb et al. were the first to investigate the emulsification of different monomer and surfactant formulations for the production of miniemulsions.[8] Using open SM elements (as opposed to SMX or KMX which are closed elements), they showed that it was possible to make droplet dispersions with average diameters of a similar order of magnitude to droplets generated using a rotor-stator and US. More recently, it has been demonstrated that SM generate narrower distributions and impose less shear than is the case with US.[7] However the emulsification process using SM is several times longer than that using US to obtain similar droplet sizes with formulations employing performed surfactants.

The focus of the present work is to study the impact of utilizing in situ generated surfactants in combination with SMX elements for homogenization. The potential for improvements to the homogenization process (i.e., a reduction in the overall emulsification time) by varying operating parameters such as flow rate and number of elements is investigated by observing droplet size evolutions, pressure gradients and energy consumption. Finally, we will investigate the feasibility of integrating a continuous tubular reactor with in-line emulsification to develop a continuous emulsification/polymerization miniemulsion process.

Experimental

Materials

The monomers used were methyl methacrylate (Aldrich, 99%) and BA (Aldrich, 99%). The costabilizer was octadecyl acrylate (Aldrich, 97%). The in situ surfactant KSA was prepared from reacting stearic acid (SA) (Aldrich, 95%) and potassium hydroxide (KOH) (Aldrich, 90%) in a 2:3 mole ratio to compensate for any hydrolysis of the stearate anion.[3] Deionised water and the water-soluble initiator, potassium persulphate (KPS) (Acros, 98%) were used for all experiments. All materials were used as received.

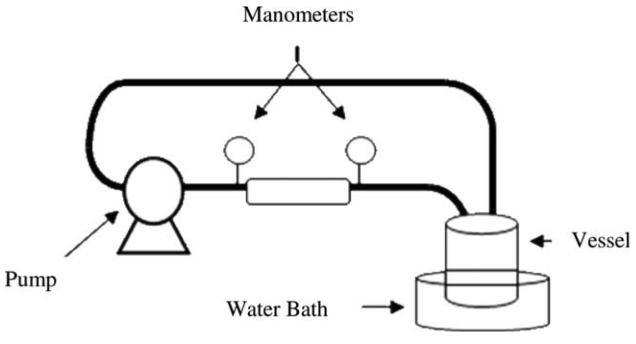

Figure 2. A: Homogenization set up for the static mixers.

A closed loop system consisting of a pump, tubing, product reservoir and temperature bath.

Homogenization

The SMX elements provided by Sulzer ChemTech. were 6 mm in diameter with six crossbars aligned at 45° to the axis of the pipe with a pitch (length to diameter ratio) of 1.0. Each element was bound at 90° to the previous element, for a total of seven elements fitted flush within a stainless steel pipe provided by Sulzer ChemTech. We will refer to seven elements within a tube as a "bank" of elements or mixers. A total of up to three banks of mixers (21 elements) were used at various points throughout our investigation. The banks of mixers were installed in a closed loop system consisting of a pump, tubing, reservoir tank and a water bath (Figure 2).

The pump used was a positive displacement gear pump from Viking Pump, controlled using a variable speed drive provided by 3M Technologies. The aqueous and organic phases were combined in a 2 L reservoir vessel and stirred for a few minutes to allow neutralization of the acid and base (the reader is referred to Ref. [3] for more experimental details). The mixture was pumped through at various flow rates ranging from 50 to 75 g/s ($Re \approx 10^2 - 10^3$) (see Table 1 for details). Small volumes of sample were removed from the reservoir intermittently. The pressure drop over the mixing bed was measured and recorded at timed intervals using manometers with ±0.5% accuracy. The manometers were placed at the entry and exit of the banks. Data is reported in terms of time and passes required to emulsify the batch of emulsion solution. A single pass is defined as the entire volume of emulsion passing through the bank(s) of elements

Table 1. Flow Rates at Varying RPM and the Time Required for a Single Pass Through 1 Bank of Elements

RPM	Calibrated Flow Rate (g/s)	Time for Entire Volume Passing Through the Mixing Elements Once (s)
350	50	8.49
400	53	8.06
450	58	7.18
500	62	6.94
550	66	6.31
600	75	5.52

Table 2. Miniemulsion Formulations Containing MMA and BA Monomer in a 50:50 w/w ratio, ODA and In Situ Generated KSA (FM 1)

Sample	DIW (g)	MMA (g)	BA (g)	ODA (g)	SA (mmol)	KOH (mmol)
FM 1	250	84	84	11.6	9.0	13.5

once. The mean time required for a single pass is based on the applied flow rate (Table 1) and the volume (Table 2). A single pass is defined as the entire volume of miniemulsion passing through the mixing elements once.

Miniemulsions were prepared according to the formulation FM 1 (Table 2). The organic phase contained monomer, costabilizer, and fatty acid. The alkali base was dissolved in the aqueous phase and KPS (0.06 wt % with respect to monomer mass) was added at the onset of the polymerization.

Polymerization

Batch polymerizations were carried out in a 1 L jacketed glass reactor equipped with a reflux condenser, a nitrogen inlet, an anchor stirrer (set at 300 RPM) and a sampling port. Dispersions were purged with nitrogen (25 minutes) and then heated to 70°C, using a thermostatted bath. Droplet size measurements were taken after purging to verify that no droplet coalescence took place. The initiator solution was injected when the reactor reached 70°C ($t = 0$ min). Samples were taken every 10 minutes for the first half hour and then every half hour for the remaining 2 hours of the experiment.

In the last phase of the investigation, a batch reaction was run without a nitrogen purge, using 0.3 wt % initiator and polymerized at 80°C. The purpose of the experiment was to simulate conditions for a continuous polymerization process where purging with nitrogen was not done. Therefore, an excess of initiator (0.2 vs. 0.06 wt %) was used to compensate for initiator radicals terminating in the presence of oxygen.

The single step emulsification/polymerization process was performed by combining the two steps (emulsification plus reaction) into an integrated process. Emulsifications were performed as previously described. After emulsification, the miniemulsions were discharged into a separate holding container (tank 2 of Figure 3) which was used as a feed storage for the tubular reactor. Emulsification continued and the valve between recipients 1 and 2 was opened as necessary to replace the feed consumed in the reactor. The initial batch of miniemulsions were quickly pumped through the tubular reactor (a step which took ~30 seconds) to fill the tubing and then the flow rate was dropped to desired flow rate using a driver with a cavity gear Micropump® head. The 200 ft of 4 mm ID PTFE tubing was arranged in several helical coils and submerged in a thermostatted bath preset to 80°C. No significant temperature gradients were expected during polymerization due to the large exposed surface area. Flow rate through the pump was set to ~12 to 13 g min^{-1}, to give a residence time of ~1 hour. An electronic balance located at the outlet was used to verify and ensure consistency in the flow rate. Samples were withdrawn at the end of the length of tubing every 10 mins for the first half hour and then every half hour for the remainder of the experiment. The continuous emulsification/polymerization process was run for a total of four residence times (4 hours).

Characterization

Droplet and particle size measurements were performed using a Malvern Nanosizer ZS. Samples were diluted with surfactant solution in concentrations above the CMC for droplet stability. For all runs, conversion was determined gravimetrically.

Results and Discussion

Effect of varying flow rate

In the initial phase of the investigation, we ran a series of emulsifications using a single bank of SMX elements (seven mixers) and formulation FM 1. The first parameter investigated was flow rate, which was varied by altering the pump speed from 50 to 75 g/s (350–600 RPM). We recorded the number of passes required to reach the minimum equilibrium stable droplet size (Figure 4) when operating in the transitional to early turbulent regime (Re ~10^3 for an open pipe).

Droplets prepared with formulation FM 1 gradually decreased in size as the number of passes through the elements increased. This is a general trend that is observed irrespective of the flow rate. Droplet size decreases after each successive pass through the elements until the asymptotic limit is reached, as indicated by the dashed line in Figure 4A.

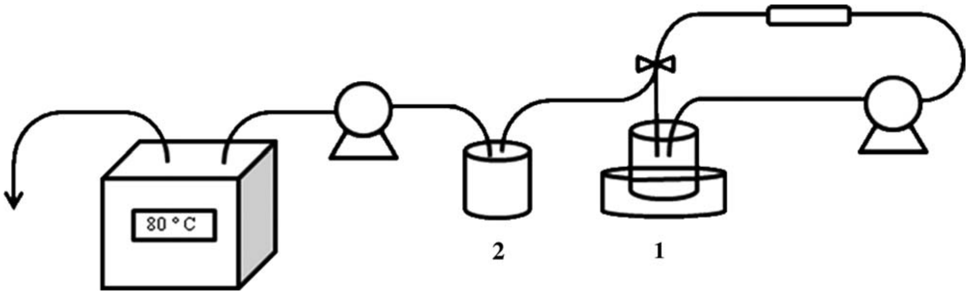

Figure 3. Continuous emulsification/polymerization process set up for the production of miniemulsions.

Set up consists of the homogenization unit as described in Figure 1 and a separate reservoir (tank 2), pump and water bath for the polymerization process.

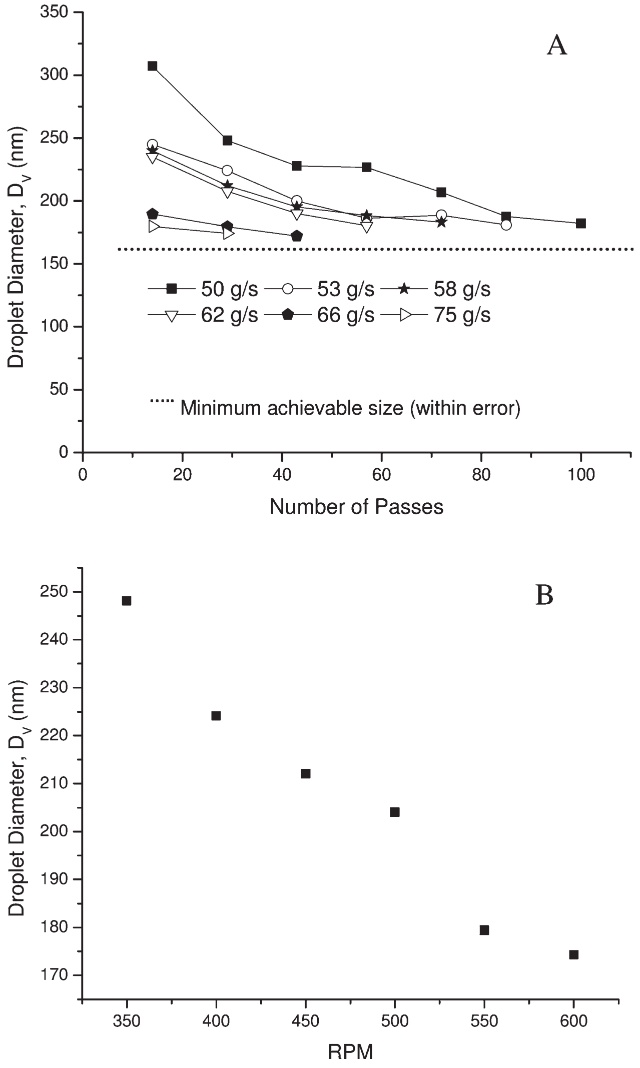

Figure 4. A: Mean droplet size evolution for miniemulsions emulsified using 1 bank of SMX elements (seven mixers) and pumped through at flow rates ranging from 50 to 75 g/s (350–600 RPM); B: Mean droplet size evolution for miniemulsions prepared with increasing RPM and ~30 passes through 1 bank of SMX mixing elements.

We believe droplet breakage within mixing elements in a turbulent regime is a hybrid of two mechanisms. Initially, multiphase streams are split into striations that get reoriented, redistributed, recombined and then are subjected to further separation. As the number of striations increases, the thickness of each striation decreases until separation becomes impossible to visually detect. As the flow rate increases and enters the transitional flow regime, it is assumed that mixing on the macroscopic scale would take place on very short time scales and it would be almost undetectable upon exiting the mixing elements. It is assumed that at the microscopic scale, the droplet breakage process proceeds with turbulent eddies breaking droplets that are larger than eddy size, until they reach the Kolmogorov length scale (the smallest eddy size).[20] This is a chaotic environment due to dramatic pressure fluctuations varying considerably from one point to the next within the elements, ultimately affecting local velocity gradients. Increasing turbulence by increasing the flow rate (W_{Breakage}) induces more droplet breakage for a given period of time and specified formulation (γ), creating smaller droplets (ΔA) as shown by Eq. 1:

$$W_{\text{Breakage}} = \gamma \times \Delta A \tag{1}$$

Emulsifying formulation FM 1 at increasing RPM for the same number of passes (~30) results in decrease in the droplet size (Figure 4B). Increasing the amount of work done on a miniemulsion results in progressively larger surface areas and hence smaller droplets. However, Figure 4A shows that the final stable droplet diameter ranges between 170 and 180 nm in size for any RPM; the only difference is the number of passes and time required to reach the equilibrium droplet diameter, which is dependent on the flow rate. The results strongly suggest that process parameters such as flow rate and formulation play a certain role in determining final droplet sizes.

For droplets ranging from μm to mm in diameter it has been computationally predicted and experimentally observed that droplets break along crossbars and cross points (intersection of crossbars) and that adjusting the number of elements along the axis and in parallel will ultimately affect the transverse flow profile of the multiphase streams. Additionally, varying the number of breaking point locations and the gaps within the crossbars will play a role in determining the droplet size evolutions. This is a reasonable explanation when dealing with "large" droplets, but one would expect that nano-sized droplets are more likely to flow around the crossbars and cross points and thus spend more time undergoing breakage due to turbulent eddies. In theory, if SMX elements are to resemble packed bed reactors, the pores constructed from the cross bars are the main channel for flow of miniemulsions and the size of the pores could determine the upper and lower limits of turbulent eddy sizes which are said to cause droplet breakage, in addition to any potential breakage along the crossbars and cross points. As shown in Figure 4A, irrespective of the flow rates, ~170 nm appears to be the lower limit of droplet size. Relating this value to the Kolmogorov length scale would require measurements of local velocity gradients along and within the perimeter of the pores, a process that is intrusive and requires specialized equipment and/or computational modeling.

It was observed that as the rotation rate of the pump head increased by 50 RPM, the number of passes required to obtain the minimum droplet size was reduced by ~14 passes through the mixing elements. However, increasing the flow rate came at a cost of higher pressure drop across the bank of elements (Figure 5).

Delivering fluid at a faster flow rate, and hence higher Reynolds number, to elements of the same size will cause a buildup of pressure at the entrance of elements (more so than at the exit which is essentially open to the atmosphere in our set up) (Figure 2). The higher the Reynolds number and hence the pressure drop, the more turbulent the environment and the more chaotic the droplet breakage process is expected to be, resulting in what appears to be more efficient

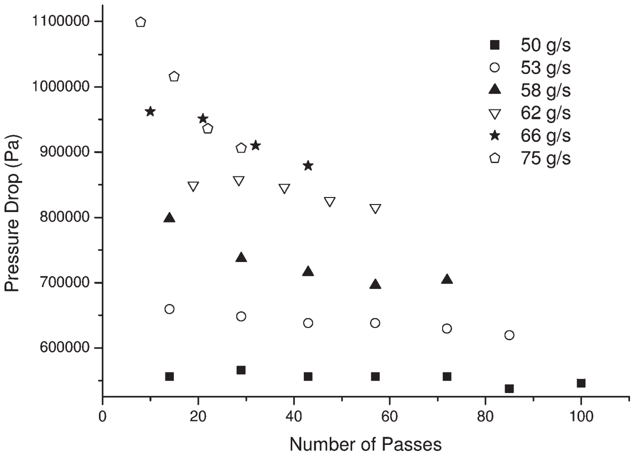

Figure 5. Pressure drop evolution for miniemulsion formulations (FM 1) emulsified at varying flow rates.

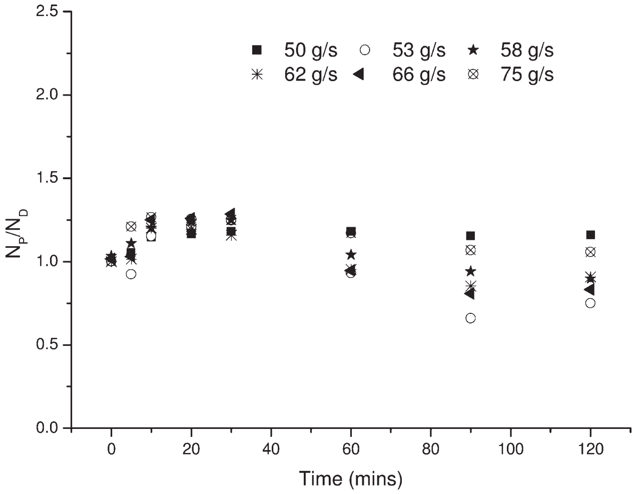

Figure 6. The ratios of the number of particles to the number of droplets throughout the polymerizations for miniemulsions prepared with 2.0 wt % *in situ* KSA and homogenized at various RPM ranging from 50 to 75 g/s.

droplet breakage, requiring fewer passages and subsequently less time. At lower flow rates (50 and 53 g/s), the pressure drop is relatively constant as the number of passes increases. As the flow rate increases, the absolute pressures across the bed increases, but decreases over a very short time span (approximately minutes) as the resistance to droplet breakage decreases (i.e., as the droplets become smaller and stabilise). A similar investigation was performed using a set of 10 mm SMX static mixers however, the pressure drop along the length of the bed ranged from 0.5 to 2 bars depending on the flow rate (50–75 g/s) resulting in ill-defined and unstable droplets. Investigations into miniemulsification with 10 mm SMX mixers at higher flow rates (>75 g/s) are scheduled for future study.

All final miniemulsion droplets prepared in this investigation were found to be stable (little variation is droplet size and distribution, ±5–10 nm) for a period of several hours and were subsequently polymerized in a batch process using water-soluble KPS as the initiator (Figure 6).

In all cases, conversion reached 85–95% within 2 hours of polymerization. Droplet diameters (D_V) were measured and used to calculate the ratio of N_P/N_D. Miniemulsions polymerized with a nearly one to one mapping of droplets to particles ($N_P/N_D = 1$ within ±5–25%). Overall, increasing the number of passes through the mixing elements generates droplets of smaller sizes. By increasing the flow rate through the mixing elements, the minimum droplet size can be attained in fewer passes but at a cost of higher pressure drop.

Increasing the number of elements in series

In the second phase of this investigation, we pose the question as to whether emulsification time can be reduced by increasing the number of elements in series, thereby reducing the amount of passes required per bank of elements. From Figure 4, we found that when operating at 50 g/s, reaching the equilibrium droplet diameter required 100 passes through the mixing elements. Therefore, in addition to the pre-existing single bank that was used in previous emulsifications, a second and third bank were added in series to bring the total of SMX mixing elements to 14 and 21, respectively. Using formulation FM 1, we ran two emulsifications at 350 RPM using 2 and 3 banks separately and recorded the time required to reach minimum equilibrium droplet size (Figure 7).

By increasing the number of elements in series, we were able to reach the minimum droplet equilibrium point significantly faster than when working with just 1 bank of elements. When emulsifying with 1 bank of elements (7 mixers), the homogenization process required a total of ~14 minutes to reach ~180 nm sized droplets. By adding an additional bank, we were able to reduce the process down to half the time (7.5 minutes). With a third bank of elements, ~180 nm droplets were produced in less than 5 minutes. The reason for the significant decrease in time is that when 2 banks are in series a total of 100 passes is achieved for one complete

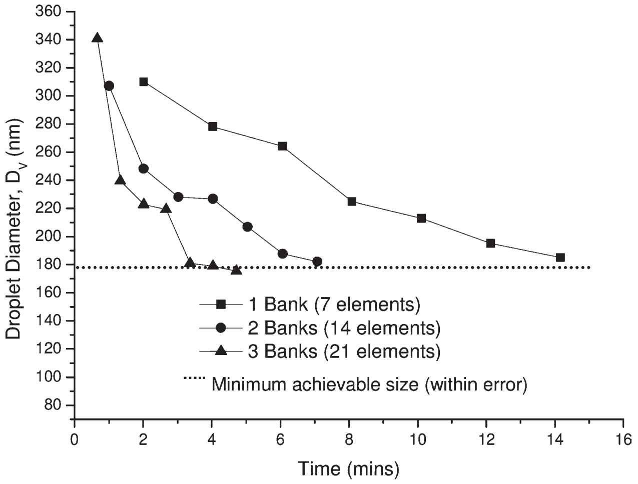

Figure 7. Mean droplet size evolution for droplets emulsified at 50 g/s using 1, 2, and 3 banks of mixers.

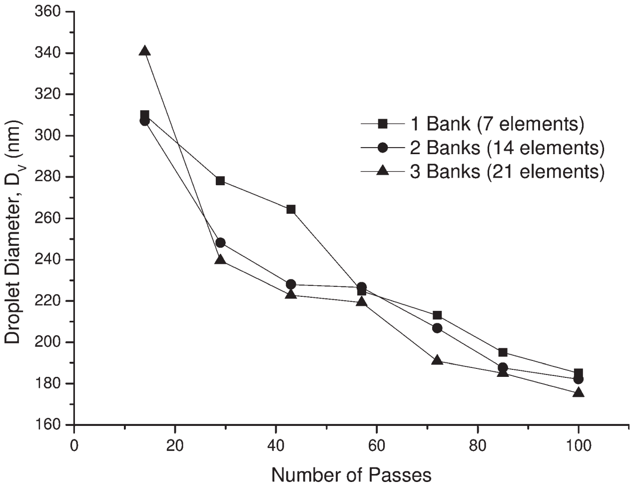

Figure 8. Mean droplet size evolution as a function of the number of passes for droplets emulsified at 50 g/s using 1, 2, and 3 banks of mixers.

circulation through the 2 banks (50 passes through each bank).Similarly, when 3 banks of elements are in series a total of ∼33 passes through each bank is required to arrive at a total of 100 passes overall. Therefore increasing the number of elements in series reduces emulsification time, so long as the number of passes required to achieve minimal droplet size is preserved (Figure 8).

As long as the total number of passes remains the same irrespective of the number of elements in series, a similar final droplet size will be attained. This trend has been reproduced at the other flow rates used in this work. As the results are very similar, they are not shown here for the sake of brevity. All final miniemulsions prepared in Figure 8 using formulation FM 1 were found to be relatively stable (little variation is droplet size and distribution) for a period of several hours and were subsequently polymerized in a batch process using water-soluble KPS as the initiator. In all cases, conversion reached 85 to 95% within 2 hours of polymerization. Droplet diameters (D_V) were measured and used to calculate the ratio of N_P/N_D. The miniemulsions polymerized with a nearly one to one mapping of droplets to particles ($N_P/N_D = 1$ within ±5–20%).

Varying both flow rate and the number of elements in series

In the previous two sections we have shown that increasing the flow rate through 1 bank of elements or the number of elements in series (to a maximum of 3 banks) can significantly reduce the emulsification time and generate droplets similar in size. The objective of this section is to investigate the combined influences of varying the flow rates though the elements and the number of elements in series.

The overall objective is to develop a process that is time, cost and most importantly energy efficient. If a process requires excessive amounts of energy, independent of its effectiveness as a homogenization device, it will not be amenable to scale up. Ideally, any device that is developed for commercial use should be scalable, reproducible and most importantly economically and energy efficient. The preceding observations have shown that in-line SMX elements are scalable in series (at least to the extent studied in this work) and generate reproducible results, irrespective of the flow rate, so long as the number of passes required to emulsify the material is maintained. The question now lies as to whether or not their energy consumption is comparable to less than more traditional devices such as RS.

The amount of power (P) (and hence energy) required to operate the SM (Figure 9), is based on the flow rate (Q) and pressure drop (ΔP) along the length of the elements Eq. 2.

$$P = \Delta P \times Q \tag{2}$$

In this study, the total work required is defined as the product of the power input and the emulsification time needed to generate droplets ranging between 170 and 180 nm. The work requirement

From Figure 9A, it is observed that as the flow rate increases, the emulsification time required to generate 170–180 nm diameter droplets drops significantly as the number

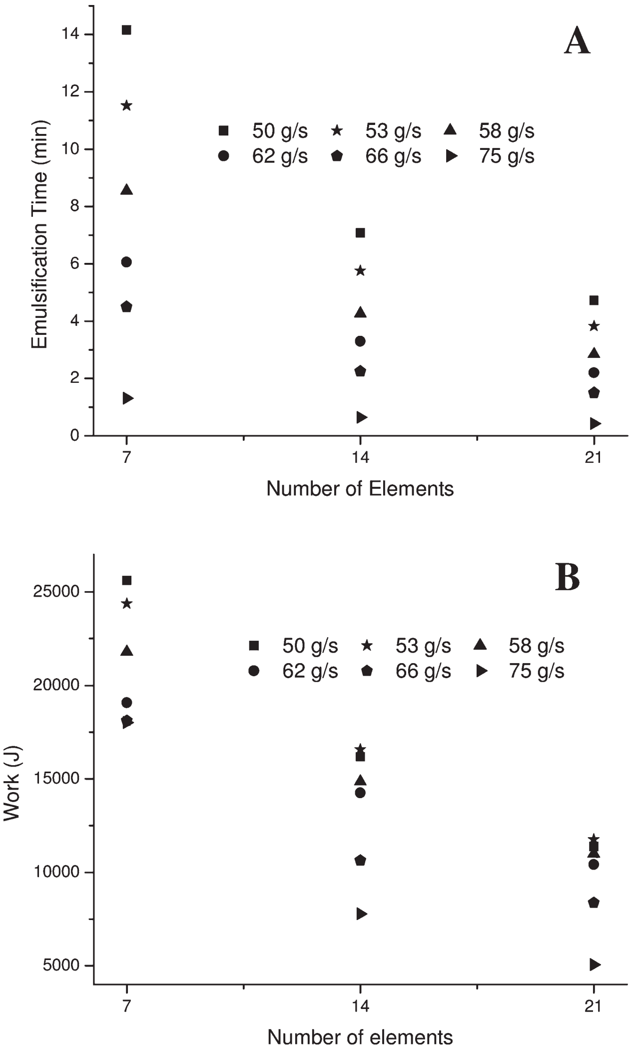

Figure 9. Time (A) and energy (B) evolution for 170 to 180 nm droplets generated at various flow rates (50–75 g/s) with varying number of elements in series.

Table 3. Estimation of the Energy Consumption Required by Ultrasonication, the Rotor-Stator and Static Mixers in the Preparation of Miniemulsion Systems

Run No.	Emulsification Device	Operating Conditions	Surfactant (2 wt %)	Droplet Diameter (nm)	Time (min)	Energy Consumption (KG/KJ)	Reference
1	Ultrasonication	80% amp.	SDBS	156	1	87	[7]
2	Rotor-stator (7.5 cm head size)	3000 RPM	SDBS	185	60	433	[7]
3	Rotor-stator (5.5 cm head size)	3000 RPM	SDBS	192	60	577	[7]
4	Rotor-stator (5.5 cm head size)	3000 RPM	*p*KSA	176	40	385	[3]
5	Rotor-stator (5.5 cm head size)	3000 RPM	In situ KSA	174	20	197	[3]
6	Static mixers (7 × 6 mm SMX)	~50 g/s	SDBS	170	30	161	[7]
7	Static mixers (7 × 6 mm SMX)	~50 g/s	In situ KSA	176	14	60	Lower limit
8	Static mixers (21 × 6 mm SMX)	~75 g/s	In situ KSA	172	0.5	12	Upper limit

2 wt % surfactant was used throughout all emulsifications.

of elements in series increases. Operating at 50 g/s with only 1 bank of elements (seven mixers) requires an emulsification time of ~14 minutes. This can be compared to operating at 75 g/s and 3 banks (21 elements), which requires ~30 seconds to reach a similar droplet size. When we increase both the flow rate and the number of elements in series, there is a significant reduction in emulsification time required to reach similar droplet sizes. Such a reduction could not be achieved by varying one parameter alone with the current set up. However, varying the two operating parameters simultaneously facilitates the emulsification process.

Similarly, as the volumetric flow rate and the number of elements in series are increased, the amount of work required to generate droplets of comparable sizes decreases by a factor of 5. It was found that ~25,000 J of work was required to generate ~170 nm droplets when operating at 50 g/s with 1 bank of mixers (seven elements), over a total emulsification time of ~14 minutes. By comparison approximately five times less work (~5000 J) was required when operating at 75 g/s with 3 banks in series (21 elements) to generate droplets comparable in size. More importantly, only 30 seconds were required representing an almost 30-fold reduction in emulsification time. This demonstrates that while operating at higher flow rates creates larger pressure drops across the banks of mixers the additional cost associated with this is more than compensated for by a very large reduction in emulsification times.

In comparison to other devices (Table 3) such as RS, it has previously been shown that emulsifying formulation FM 1 required ~20 minutes to generate ~170 nm sized droplets (Run 5).[3] The emulsification process consumes a total of $\sim 8.2 \times 10^4$ of work which utilises ~17 times more energy in comparison to working at the upper limit of our SM process of 75 g/s with 3 banks in series (Run 8) or ~3 times more at the lower limit (Run 7). Additionally, when preparing miniemulsions using SM and in situ KSA at the lower limit of our SM set up (Run 7) we are consuming ~2 to 3 times less energy than when using SDBS under similar SM conditions and nearly 7 to 10 times less compared to systems prepared with the rotor-stator (depending on rotor-stator head size). Overall, the SMX elements are more energy efficient. They are more effective at breaking down larger droplets due the even spread and breakage of the flow stream across the width of the elements, thereby generating narrower distributions, in a reasonable amount of time.

Continuous emulsification/polymerization of miniemulsions

The ability to continuously generate miniemulsions that could be immediately polymerized would have a number of advantages, including eliminating the need to store and transport intermediate emulsions, and to exploit the numerous advantages inherent in a continuous process.[21,22]

The choice of reactor is important in this context, and while many options are open, the use of continuous stirred tank reactors (CSTR) is not recommended because the wide residence time distribution would lead to the inclusion of unpolymerized droplets in the exit stream. For this reason, either (semi-)batch reactors or continuous tubular reactors seem to be better choices since all of the particles in the reactor will have the same residence time. To exploit the advantages of a continuous system, we will focus on the use of a linear flow tubular reactor.

Linear tubular reactors are simple to design and construct, can operate for an extended period of time with very little maintenance, and have large surface area to volume ratio which allows for efficient heat removal. Previous studies have demonstrated successful polymerization of miniemulsions using tubular reactors on a laboratory scale.[23,24]

The goal of the final step of our investigation is to develop a process whereby miniemulsions are continuously produced and polymerized on a laboratory scale. A schematic illustration of the set up is shown in Figure 3. The organic and aqueous phases are introduced into the emulsification vessel and emulsified for the appropriate number of passes (depending on flow rate). Working at 75 g/s and 3 banks of elements in series requires ~30 passes to emulsify ~0.4 L of a mixture of water and monomer (FM1). As described above, an initial emulsification step is used to fill up a holding tank situated between the emulsification loop and the reactor, and to fill the reactor itself. Once both the reactor and the holding tank are full, a second gear pump is used to pump the stable miniemulsion from the holding tank through the tubular reactor at a flow rate of ~12 g/min (this corresponds to a residence time of 1 hour in the tube). Given the difference between the residence time of the reactor and the time required to generate the emulsion, it is rather straightforward to occasionally open the T-valve between the emulsification loop and the holding tank to ensure that the latter always contains enough emulsion to keep the tubular reactor full. Due to the nature of the set up, purging with

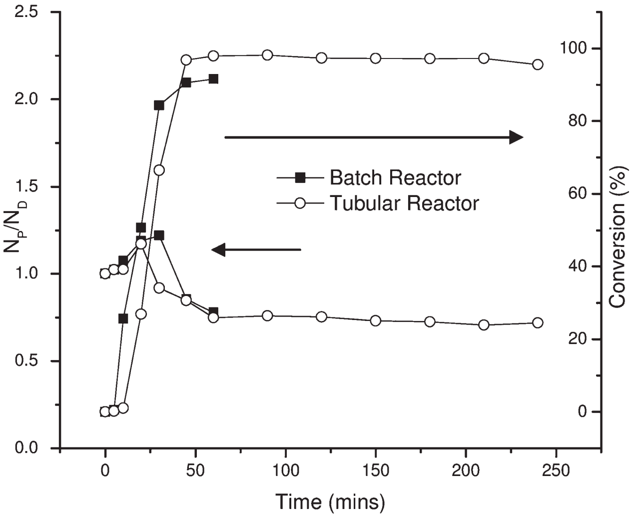

Figure 10. Conversion and N_P/N_D profiles for miniemulsions emulsified in the static mixers at 75 g/s with 3 banks of elements in series and polymerized in a batch (■) or one step emulsification/ polymerization process with a tubular reactor (○).

nitrogen proved difficult and so an excess amount (0.2 wt % with respect to monomer mass) of initiator was used at a slightly elevated temperature compared to our previous polymerization experiments (80 vs. 70°C). The tubular reactor process was compared to a batch polymerization also operated with excess initiator and at 80°C (Figure 10).

Both the continuous and the batch processes were initiated using water-soluble KPS. In both cases, conversion reached between 90 and 97% within 1 hour of polymerization. Droplet diameters (D_V) were measured and used to calculate the ratio of N_P/N_D, which is ~0.8 for both the batch and continuous reactors. The batch process was stopped after 1 hour while that of the one step continuous emulsification/polymerization process was left to run for 4 hours (four residence times). It can clearly be seen here that the continuous process is stable.

Comparing the novel continuous approach we developed with a conventional batch approach we observe similar reaction profiles both in terms of conversion and droplet/particle nucleation. This has a wide range of implications, both in terms of the ability to control product quality as well as the efficiency of production and control of the reaction kinetics and conversion. In previous works from our group, it has been demonstrated that changing the surfactant concentration allows one to change the particle diameters rather easily. In addition, this set-up allows one to work at different solid contents or formulations without needing to shut down the reactor.

Conclusions

The work presented here demonstrates that SMX static mixer elements can be used to effectively and efficiently create polymerisable miniemulsions. The rapid stabilization of the droplets generated in this manner due to the acid/base neutralization reaction that forms the surfactants at the surface of the particle means that this emulsification can be done more rapidly with the in situ surfactant than with preformed surfactant that must diffuse to, then absorb on the droplets.

Furthermore it was shown that the reduction in the time required to produce a stable emulsion for high flow rates and an increased number of mixing elements more than compensated for the higher pressure in the emulsification loop. In other words, although the instantaneous energy requirements were greater at 75 g/s with 21 mixing elements than they were at g/s and seven elements, the time required to create the emulsion was 15 times shorter for the former configuration.

Subsequently, a continuous process for polymerization of miniemulsions was studied at the laboratory scale using in situ surfactants with 3 banks of SMX mixer elements (21 total elements). Comparing this process with a batch process, similar results for the N_P/N_D ratio and conversion were obtained, but the continuous process was accomplished in a single step. This novel approach offers important opportunities for improved efficiency when studying processes at the laboratory scale and may be a feasible approach for industrial polymerization processes.

Literature Cited

1. Taylor P. Ostwald ripening in emulsions. *Adv. Coll. Interfacial Sci.* 1998;75:107–163.
2. Ferri JK, Stebe KJ. Which surfactants reduce surface tension faster? A scaling argument for diffusion-controlled adsorption. *Adv. Coll. Interface Sci.* 2000;85:61–97.
3. El-Jaby U, Cunningham MF, McKenna TFL. The advantages of in situ surfactant generation for miniemulsions. *Macromol. Rapid Commun.* 2010;31:558–562.
4. Richardson ES, Pitt WG, Woodbury DJ. The role of cavitation in liposome formation. *Biophys. J.* 2007;93:4100–4107.
5. Manea M, Chemtob A, Paulis M, de la Cal JC, Barandiaran MJ, Asua JM. Miniemulsification in high-pressure homogenisers. *AIChE J.* 2008;54:289–297.
6. El-Jaby U, Cunningham M, Enright T, McKenna TFL. Polymerisable miniemulsions using rotor-stator homogenisers. *Macromol. React. Eng.* 2008;4:350–360.
7. El-Jaby U, Cunningham M, McKenna TFL. Comparison of emulsification devices for the production of miniemulsions. *Ind. Eng. Chem. Res.* 2009;48:10147–10151.
8. Ouzineb K, Lord C, Lesauze N, Graillat C, Tanguy PA, McKenna T. Homogenisation devices for the production of miniemulsions. *Chem. Eng. Sci.* 2006;61:2994–3000.
9. Zalc JM, Szalai ES, Muzzio FJ. Characterisation of flow and mixing in an SMX static mixer. *AIChE J.* 2002;48:427–436.
10. Fradette L, Li HZ, Choplin L. 3D finite element simulation of fluid flow through a SMX static mixer. *Comput. Chem. Eng.* 1998;22: S759–S761.
11. Rauline D, Le Blévec JM, Bousquet J, Tanguy PA. A comparative assessment of the performance of the kenics and SMX static mixers. *Trans IChemE.* 2000;78:389–396.
12. Heniche M, Tanguy PA, Reeder MF, Fasano JB. Numerical investigation of blade shape in static mixing. *AIChE J.* 2005;51: 44–58.
13. Rauline D, Tanguy PA, Le Blévec JM, Bousquet J. Numerical investigation of the performance of several static mixers. *Can. J. Chem. Eng.* 1998;76:527–535.
14. Morancais P, Hirech K, Carnelle G, Legrand J. Friction factor in static mixer and determination of geometric parameters of SMX sulzer mixers. *Chem. Eng. Comm.* 1999;171:77–93.
15. Legrand J, Morancais P, Carnelle G. Liquid-liquid dispersion in an SMX sulzer static mixer. *Trans IChemE.* 2001;79:949–956.
16. Das PK, Legrand J, Morancais P, Carnelle G. Drop breakage model in static mixers at low and intermediate Reynolds numbers. *Chem. Eng. Sci.* 2005;60:231–238.

17. Liu S, Hrymak AN, Wood PE. Drop breakup in an SMX static mixer in laminar flow. *Can. J. Chem. Eng.* 2005;83:793–807.
18. Liu S, Hrymak AN, Wood PE. Design modifications to SMX static mixer for improving mixing. *AIChE J.* 2006;52:150–157.
19. Singh MK, Anderson PD, Meijer HEH. Understanding and optimizing the SMX static mixer. *Macromol. Rapid Commun.* 2009;30:362–376.
20. Walstra P. Turbulence depression by polymers and its effect on disruption of emulsion droplets. *Chem. Eng. Sci.* 1974;29:882–885.
21. González I, Paulis M, de la Cal JC, Asua JM. (Mini)emulsion polymerisation: effect of the segregation degree on polymer architecture. *Macromol. React. Eng.* 2007;1:635–642.
22. Asua,JM.*Introduction to polymerisation processes*. In: Asua JM, editor. *Polymer Reaction Engineering*.Oxford:Wiley-Blackwell Publishing Ltd,2009:1–28.
23. Schork FJ, Guo J. Continuous miniemulsion polymerisation. *Macromol. React. Eng.* 2008;2:287–303.
24. Ouzineb K, Graillat C, McKenna TF. Continuous tubular reactor as a seed reactor in miniemulsion polymerisation. *DECHEMA Monographien.* 2001;137:293–301.

Manuscript received Feb. 4, 2010, revision received May 2, 2010, and final revision received Jun 30, 2010.