

Miniemulsions Using Static Mixers: A Feasibility Study Using Simple In-Line Static Mixers

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ABSTRACT: The feasibility of using simple static mixers (SM) to produce polymerisable miniemulsion dispersions, and the influence of the emulsification conditions on the diameter of the resulting methylmethacrylate droplets were examined. It was shown that these simple mixers could be used to generate droplets with diameters on the order of 150–300 nm, and that these droplets could be successfully polymerised. As expected, increasing the flow rate through the mixers led to a decrease in the average droplet size. Doubling the number of mixers in series did

not have a significant influence on the droplet size but did decrease the time needed to achieve a steady final value of the average diameter. On the contrary, changing the surfactant concentration had an observable effect on the droplet sizes obtained, with higher surfactant concentrations yielding smaller droplets. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3875–3881, 2009

Key words: miniemulsion; static mixer; droplet size; free radical polymerisation

INTRODUCTION

Polymerisable miniemulsions are typically created by dispersing a monomer rich phase (oil) in aqueous phase using a mechanical homogenisation device such as an ultrasonic dismembrator, or, more recently, a high pressure homogeniser (HPH)¹ or microfluidiser, or rotor-stator mixer.² Sonication is obviously well-adapted for laboratory use, but is not a convenient technique for scale-up to commercial volumes. It has been shown that HPH can be an effective means of making miniemulsions, and because such devices are used in numerous industrial applications, they have the potential to be used on industrial scales. Alternatively, Ouzineb et al.³ demonstrated the feasibility of making miniemulsions using a rotor-stator and SM. They showed that very simple static (or motionless) mixers, which have been used for more than 30 years⁴ in the chemical process industry, are viable alternatives to the aforementioned techniques for the production of miniemulsions because of their low energy consumption and the relatively low shear that they impose on the phase being dispersed. It was found that only a small amount of the total energy developed by any of the homogenisation devices

considered in their study³ (they compared an ultrasonicator, a rotor-stator, and a static mixer) is efficiently devoted to definite droplet rupture (the rest is lost to heat and coalescence). In their study, it was shown that 1–4% of the energy used in the process was used to irreversibly form the droplets. This can obviously be improved upon, but still compares favorably with efficiencies of 0.002–0.007% for rotor-stators and sonication. It is likely that these efficiencies are specific to the experimental conditions used in the study, but they do show the interest of using SM to this effect. In addition, it also turns out that the temperature rise during the emulsification step is much lower with SM than it is with a rotor-stator mixer or ultrasonication.⁵

SM are made of elements of an appropriate shape, arranged in a repetitive fashion, and generally placed in a tube. A fluid is made to flow over a series of mixing elements which have the effect of accelerating, dividing and recombining the liquid to achieve either a high degree of mixing with little energy, or to effectively disperse one fluid in another.⁴ More than 30 commercial types of SM are currently available, with varying forms and dimensions.⁶ Gyenis⁷ presented an overview of the working principles, mechanism, performance, modeling, and applications of SM. The interested reader is referred to this work for further details about the use of SM.

However, despite their wide spread use for numerous applications, it appears that very little information on droplet formation on the scale of hundreds of nanometres used in latex production is available. In their preliminary study, Ouzineb et al.³ concentrated

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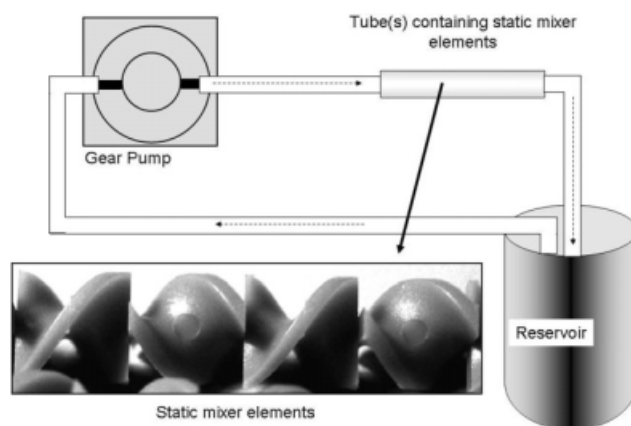


Figure 1 Schematic representation of a static mixer setup. The reservoir is mixer with a magnetic stirrer.

on showing that SM are a plausible means of generating droplets of the required size for miniemulsion processes. They did not explore the role of different process conditions such as the flow rate and number of mixing elements on the droplet size, nor did they look at whether or not the droplets thus obtained could be polymerised. This article will continue with an exploration of these aspects of the use of SM in the production of miniemulsions, and will lay the ground work for more detailed future studies.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, 99%), butyl acrylate was supplied from ACROS. *N*-Hexadecane (HD, 99%), sodium dodecyl sulfate (SDS, 99%), and ammonium persulphate (APS) were all obtained from ACROS and used as supplied. Deionised water was used as the continuous phase.

Miniemulsification procedure

Miniemulsions were prepared by dissolving the surfactant (SDS) in deionised water in one beaker (0.14 g SDS in 70 g water), and mixing the hydrophobic agent (HD) in the monomer (MMA) in another beaker (28.1 g MMA and 1.4 g HD). These mixtures were stirred separately. Then, the organic phase was added to the aqueous phase under gentle agitation with a magnetic stirrer. Finally, the mixture was homogenized by causing it to circulate over one or more tubes with an interior diameter (ID) of 1 cm and a length of 100 cm, each containing 4 static mixing elements 15 cm in length and 6.4 mm in diameter. Figure 1 shows a general configuration of SM in which the mixture of the two phases is placed in a reservoir with a magnetic stirrer, and then circulated through a tube (or tubes) containing the SM ele-

ments. The flow rate was fixed at 60.6 mL/s for all the experiments unless otherwise noted.

The intensity average droplet size and polydispersity of miniemulsions were measured with a Malvern Autosizer. The miniemulsions were considered stable if there was no change (within estimated experimental error of 10 nm) in the average droplet size after approximately 4 h.

Miniemulsion polymerisation

The miniemulsion polymerisations were carried out in a cylindrical glass batch reactor (150 mL) with a nitrogen inlet for all the samples. After introduction of the miniemulsion into the reactor, nitrogen was bubbled through the solution for 30 min to eliminate the oxygen before beginning the polymerisation process. Once this step completed, the mixture is brought to the desired reaction temperature and the initiator, APS is added to the batch.

The reactor contents were mixed during polymerisation with a glass anchor stirrer at a constant speed of 250 rpm and the temperature was kept constant at 70°C, using water circulation from a thermostatic bath. Samples were periodically withdrawn to follow the particle size and size distribution, as well as conversion which was measured by gravimetry.

RESULTS AND DISCUSSION

The effect of flow rate on droplet diameter

The droplet diameter of unpolymerised MMA miniemulsions was evaluated as a function of time for three different flow rates in the SM assembly shown in Figure 1, and the results are shown in Figure 2. It can be seen from Figure 2(a) that the droplet diameter decreases asymptotically toward a limiting value with increasing homogenisation time, and that the limiting droplet size depends on the flow rate. As one would expect, the higher the flow rate is, the smaller the droplet diameter. This is obviously because of the higher levels of energy dissipation at higher flow rates—in other words the shear stress imposed on the droplet during homogenisation is greater when the velocity is greater. The evolution of the polydispersity index (PI) furnished by the software of the ZetaSizer 1000[®] can be seen in Figure 2(b). It should be pointed out that this index is a number provided by the software after the measurement and is taken as an indication of the narrowness of the distribution in question. Discussions with the manufacturer have led to the conclusion that a distribution with a PI less than 0.1 can be considered monodisperse, whereas values above this limit indicate that the PSD or DSD can be considered broad, and one cannot use the average particle size with

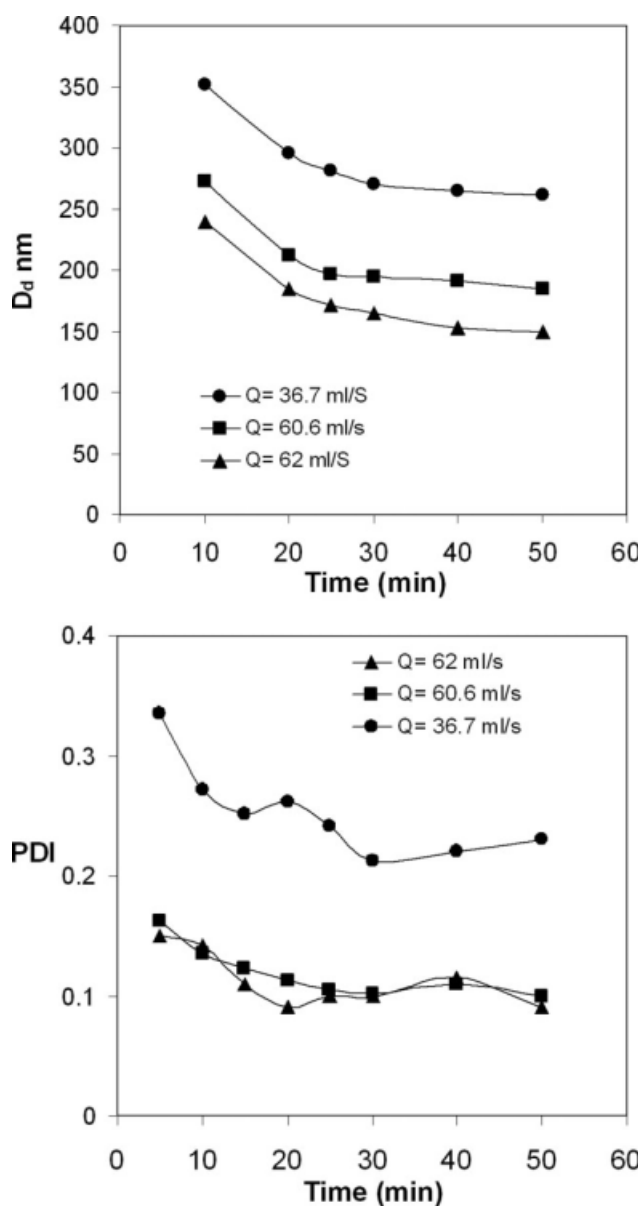


Figure 2 Evolution of droplet size (a - top) and polydispersity index (b - bottom) as a function of homogenisation time at different flow rates of 62.2, 60.6, and 36.7 mL/s.

confidence. As we can see here, the two higher flow rates level off to steady values of the PI of close to 0.1 after ~ 20 min of emulsification. This, plus the lower particle size that can be obtained at the high flow rates are the reasons for which it was decided to use a flow of 60.6 mL/s in the rest of the work (the pump was at its maximum capacity at 62.2 mL/s and did not deliver a steady flow in all cases).

The repeatability of the nanodroplet formation in stable miniemulsions has been investigated by repeating the emulsification process with the SM, under identical conditions and the results are shown in Figure 3. The results show that the droplet diameter varies by less than 10 nm from one sample to

another, and we can consider that the process of emulsification in this manner is repeatable.

Miniemulsion polymerisation of MMA nanodroplets

The miniemulsion polymerisation was carried out according to the procedure described above. The evolution of the monomer conversion and particle because as a function of time for droplets made at two different flow rates can be seen in Figure 4. As can be seen, the reaction rate appears to be slightly slower for the droplets made at 37 mL/s than for 60.6 mL/s. This is presumably because of the fact that the droplets obtained at the lower flow are larger [see Fig. 4 (b)], and thus offer a lower surface area for the capture of free radicals. However the major difference between the two appears to be the evolution of the particle size as a function of the polymerisation time: in the run done with droplets generated at 37 mL/s, there is an apparent renucleation of particles (drop in size corresponds to an increase in number), followed by coalescence of the particles to yield particles larger than the original droplets. This loss of control is associated with an increase in the polydispersity index of the droplets, which as shown above is higher for the lower flow rates. Experience has shown⁸ that when the PDI is too high, we appear to have a competition between nucleation characteristic of conventional emulsion polymerisation and polymerisation of the miniemulsion. The system shown in Figure 4 supports this following scenario: nucleation of new particles leads to a reduction of free surfactant (the surfactant

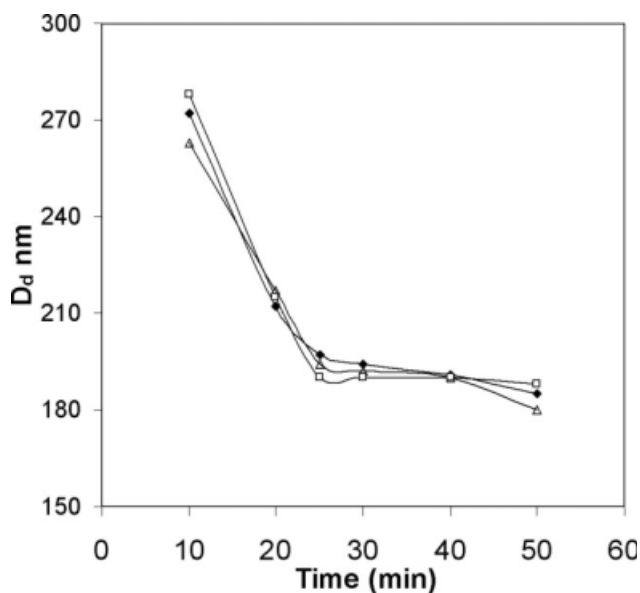


Figure 3 Repeatability of the formation of nanodroplets via SM at a flow rate of 60.6 mL/s and using one bank of SMs elements.

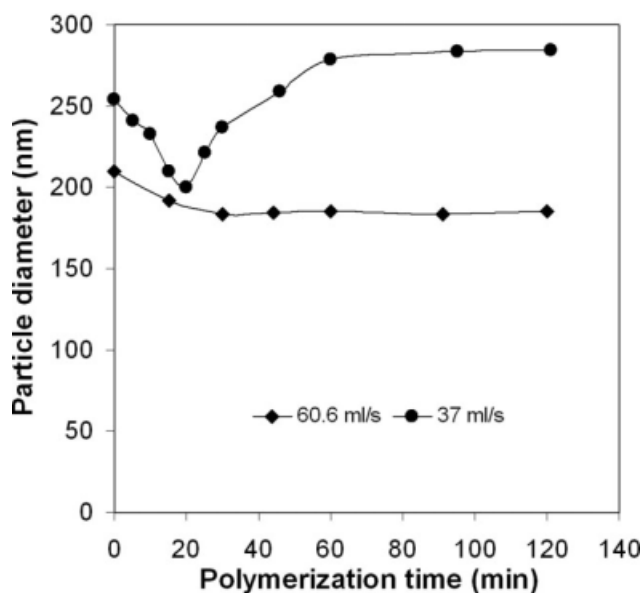
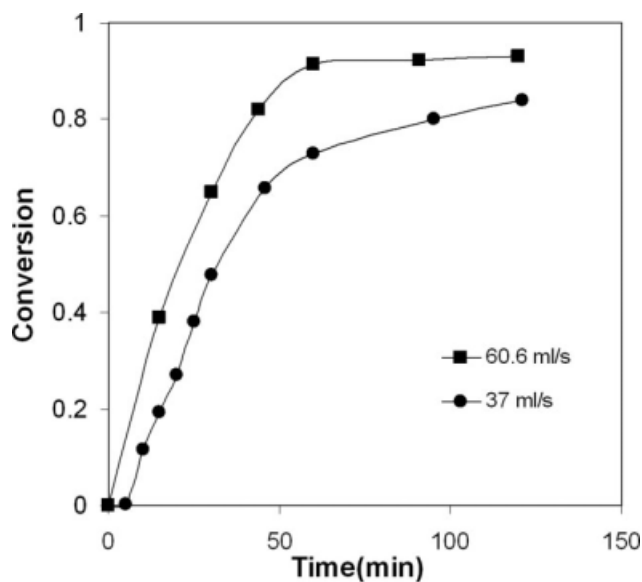


Figure 4 Conversion of polymerisation (a) and evolution of the average particle size (b) as a function of polymerisation time for miniemulsions created at different flow rates with one bank of SMs and using the reference recipe defined above.

present in the water phase is consumed to stabilize the newly formed particles) in the reactor; continued growth of new particles leads to the creation of new surface area that cannot be sufficiently stabilized leading to the partially controlled coalescence of the particles during the reaction.

The effect of surfactant concentration on creation of nanodroplets

MMA dispersions containing surfactant concentrations of 0.5, 1.4 (reference value), 2, and 3 g/L were made using the procedure described above (the

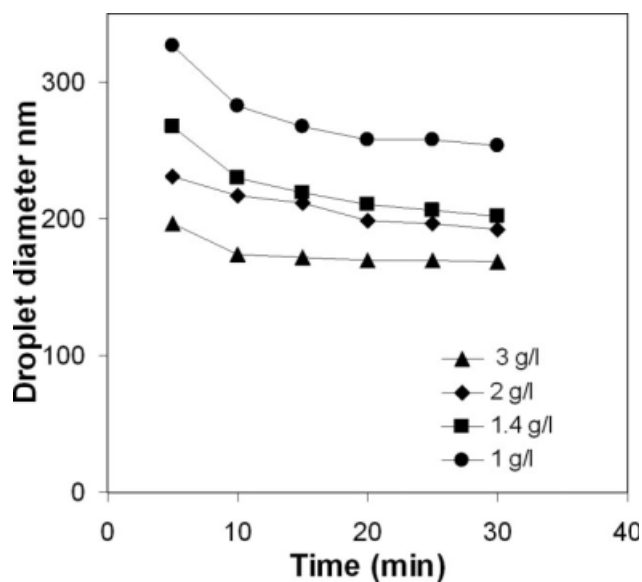


Figure 5 Evolution of average droplet size as a function of homogenisation time for different SDS concentrations using one bank of SMs and a flow rate of 60.6 mL/s.

CMC of SDS was measured by conductimetry and found to be 1.8 g/L in pure deionised water at 25°C). The evolution of the droplet size is shown as a function of homogenisation time in Figure 5.

Once again, as one might expect smaller droplets are obtained at higher surfactant concentrations, and it appears that the limiting particle size is also reached more quickly at higher surfactant concentrations. The evolution of the final droplet size as a function of the total amount of surfactant in the

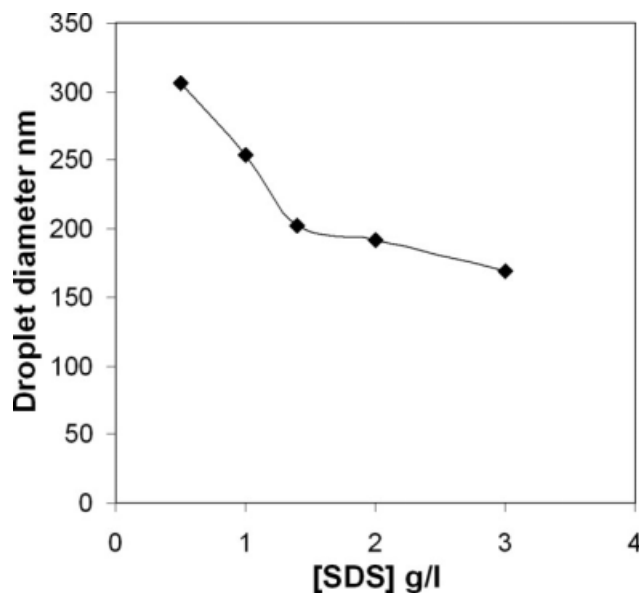


Figure 6 The effect of SDS concentration on final droplet diameter using one bank of SMs and a flow rate of 60.6 mL/s.

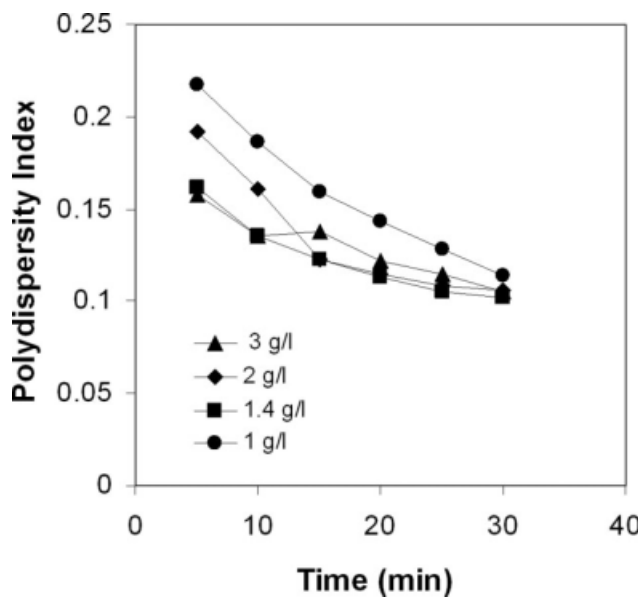


Figure 7 The effect of homogenisation time on polydispersity of nanodroplets.

recipe is shown in Figure 6. It is interesting to note that the final droplet size attainable appears to level off at concentrations of SDS greater than or equal to 2 g/L (here, close to the CMC although without further study it is difficult to know whether or not this is simply a coincidence) using the current set-up. This suggests that below this concentration, reducing the interfacial tension plays a significant role in determining the droplet size. Above this limit, one might suspect that it is the amount of energy dissipated by the mixing device that is more important. Clearly one would not expect the changes in D_d to vary linearly with the concentration of surfactant above a certain level since it is necessary to create surface area using mechanical energy before the droplets need to be stabilized. It appears that the surface area generated in these experiments can be sufficiently stabilized by about 2 g/L of SDS, and that adding more surfactant does not change the limiting value here.

The polydispersity of miniemulsions was monitored during the miniemulsification and the results are shown in Figure 7. It is interesting to note that it takes a longer time for the PDI to stabilize than it does for the average size to stabilize. The reason for this is not clear at the present time. It is possible that this is because of the mechanism of droplet reduction in the SM, and might be caused for instance by a slow reduction of a small number of larger droplets. In this case, one would reach an average size that changes little after a given time, but the droplet size distribution would continue to narrow as the large droplets were broken up and stabilized. Of course, this hypothesis needs to be

tested in a future paper before any strong conclusions can be drawn.

The stability and aging of the miniemulsions were investigated by measuring the droplet diameter and PDI at 30 min and 4 h after miniemulsification on one bank of SMs at a flow rate of 60.6 mL/s for the different surfactant concentrations considered in this work (four hours was chosen somewhat arbitrarily, but essentially because it is assumed that the droplets would be used within a few hours of their generation in an industrial setting). The results are shown in Figure 8 where it can be seen that the

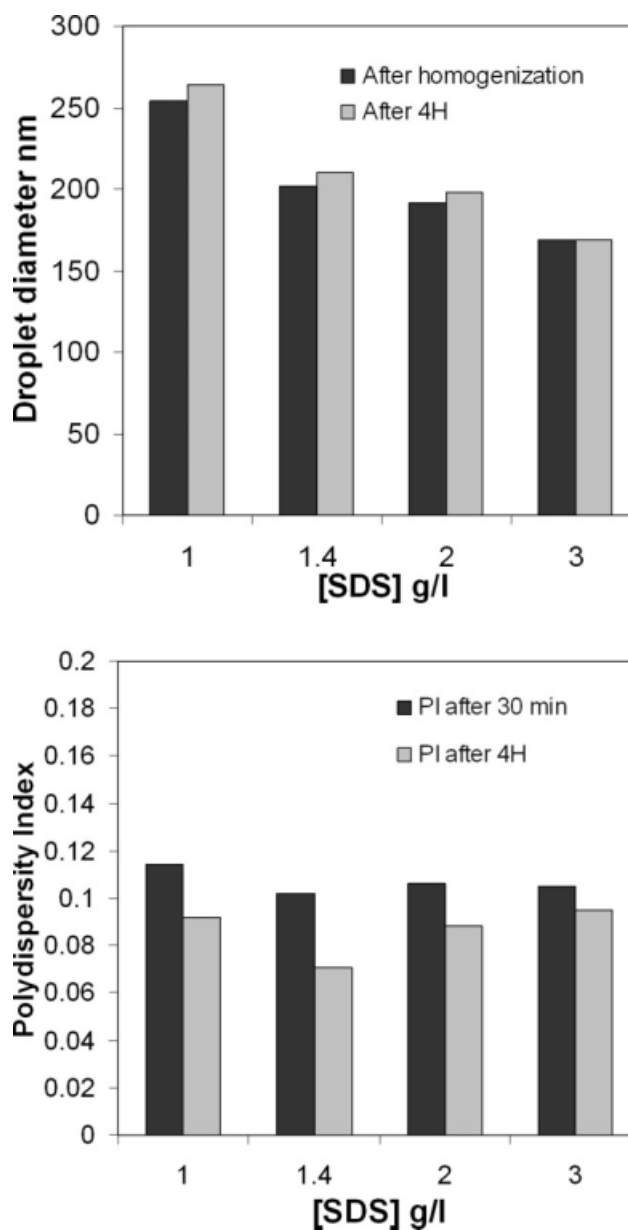


Figure 8 The effect of SDS concentration on miniemulsion stability: (top) evolution of average droplet size at 30 min and 4 h after homogenisation; and (bottom) evolution of the Malvern PDI at 30 min and 4 h after homogenisation.

variation of droplet diameter is not significant over the course of 4 h. For example, the variation of droplet size for the samples containing 1.4 g/L SDS was only 9 nm. This is close to what we accept as the limit of experimental variability of the particle size analyser used in this work, so it is difficult to affirm the tendency seen in Figure 8: a slight increase in the average diameter from 30 min to 4 h, with a slight narrowing of the PSD. This observation would be consistent with a small amount of Ostwald ripening of the emulsified dispersion.

Comparison with ultrasound

Two series of samples were emulsified by SM and US, using the reference recipe defined above. A high-Intensity ultrasonic processor (Branson, model CV26) of 600 W was used at 80% of power. The results showed that with the same recipe, homogenisation of MMA using US for 120 second leads to smaller droplets (130 nm) compared to a miniemulsion created by SM during 30 min with a flow rate of 60.6 mL/s and one bank of SM (212 nm). Both emulsions were found to be stable and there is no significant change in their droplet size after 4 h (less than 10 nm variation).

The stable droplets were polymerised using APS as the initiator at 70°C. It can be seen from Figure 9 that the particle diameter decreases slightly for miniemulsions created by SM, but that in both cases the size remains fairly stable throughout the polymerisation. The major difference between the two systems appears to be the difference in initial droplet size, which is smaller with US than with the SM used in

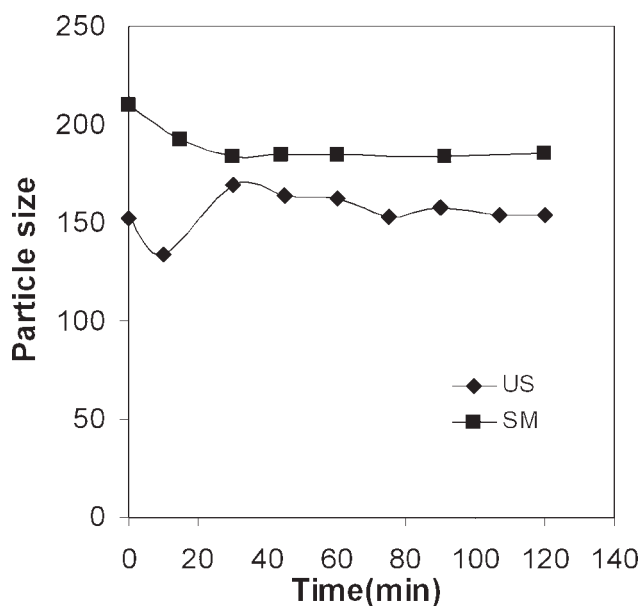


Figure 9 Impact of homogenisation device on the droplet size and evolution of particle size at 70°C.

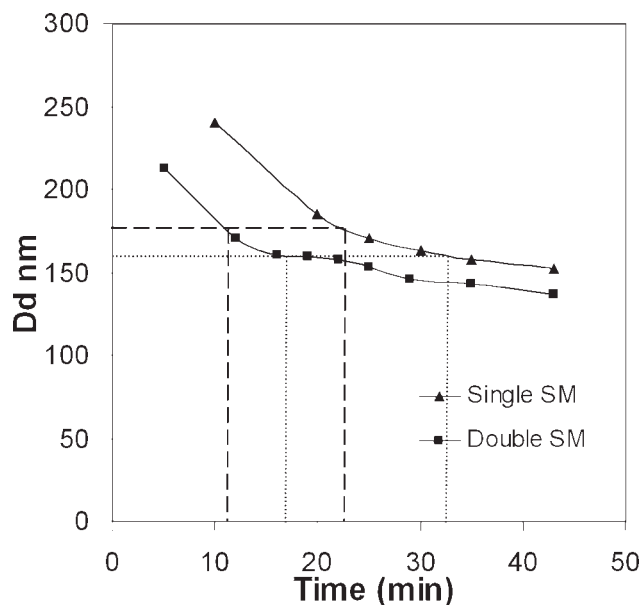


Figure 10 The effect of the number of SMs on droplet diameter with a flow rate of 60.6 mL/s for using the reference recipe given in the experimental section.

this work. This is attributable to the much more intense mixing (higher levels of energy dispersion) offered by the ultrasonic dismembrator.

The effect of the number of SMs

The effect of the number of SM elements on droplet break up was investigated at the flow rate of 60.6 g/s using the reference recipe cited above, but this time using two tubes in series containing mixing elements in series, one immediately after the other (in other words, the number of times the fluid to be dispersed passed over the mixing element was double). The results are shown in Figure 10. It can be seen here that the droplet formation process is more rapid, with the average size reaching a plateau sooner than with a single bank of SM. It should be noted that no observable difference was seen in terms of polydispersity for the two series of experiments. In addition, if we compare the times taken to reach droplet sizes of 180 nm, and then 160 nm, it can be seen that it takes almost exactly twice as long with one set of mixing elements as with two. In other words, it appears that it is the number of passes over the elements that counts, rather than time of emulsification. In addition, this also implies that there is not an appreciable amount of coagulation in the reservoir shown in Figure 1.

CONCLUSION

We have shown in this article that it is possible to form stable MMA nanodroplets using SMs as homogenisation device. It was found that the

average droplet size could be varied by changing the flow rate and the surfactant concentration. As one might expect, droplet size decreases as both of these quantities increase. However, it was also shown that higher flow rates are required to obtain a DSD that is sufficiently narrow that it can be polymerised to obtain a reasonable one-to-one copy of droplets to particles.

Doubling the number of mixing elements allowed us to obtain very similar stable droplets more quickly than for a single set of elements with the experimental set-up used here.

Finally, the major focus of this work was to demonstrate the feasibility of using SM to generate polymerisable dispersions of droplets. A comparison of emulsification with the SM set-up used here and ultrasonication strongly suggests that increasing the intensity of the mixing process will lead to smaller droplets. This can be done using stronger pumps giving higher flow rates, and also changing the

geometry of the mixers. A future article from this group will focus on using different types of mixing elements and flow conditions to obtain miniemulsions in this manner.

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