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Miniemulsification: An Analysis of the Use of Rotor Stators as Emulsification Devices

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Summary: Production of polymeric latexes by miniemulsion techniques is clearly attracting more and more attention for a number of reasons. However, one of the limiting factors in the acceptance of miniemulsion polymerisation as a commercialisible technique was that in early laboratory studies ultrasonication was the only method considered for the generation of polymerisable droplets. It is shown in the current paper that rotor stator mixers are an promising alternative. In addition to demonstrating the feasibility of these techniques, an investigation of the evolution of the particle size distribution during polymerisation revealed that controlled coalescence can occur for reasons that are difficult to identify.

Keywords: emulsification; miniemulsion polymerisation; rotor stator mixers; static mixers; tubular reactors

Introduction

The production of polymers via free radical polymerisation in colloidal dispersions continues to be of economic significance for a number of reasons including: a desire to substitute current solvent-based systems with an aqueous medium for environmental reasons; a reduction in the bulk viscosity of the reactor contents (better heat transfer, easier handling); and the ease of manipulation of sticky or film forming materials. Traditionally a large majority of such products have been made by suspension and conventional emulsion polymerisation.

More recently, the ease with which one can incorporate a wide range of organic and inorganic materials into the final product, as well as the ability to directly produce and emulsify dispersions with solids contents of up to 50 or even 60 volume per cent[1] have made miniemulsions more and more attractive as an alternative means for production of heterogeneous aqueous dispersions of polymer particles.[2]

Miniemulsion droplets, with diameters typically on the order of 100–500 nm, are created by mechanically dispersing an organic phase in an aqueous medium. The key components contributing to the stability of the miniemulsion droplets are the surfactant which prevents coalescence and the co-stabiliser which reduces the rate of Ostwald ripening.[3] When the polymerisation proceeds via a free radical mechanism, nucleation takes place in the monomer droplet. Thus either water-soluble, or oil soluble initiator can be used.[4–6]

The dispersion of the droplets, and to a large extent the size of the polymerisable mini-emulsion droplets will be determined by the chemical components of the stabilisation system, the nature of the monomer(s) being emulsified (hydrophobic monomers will form larger droplets than hydrophilic ones all other things being equal), and most importantly the type of mechanical deviceused for the emulsification step.[7] Various homogenization devices can be used, with the most common at the laboratory scale being ultrasonic probes. However such devices are, on the whole, not practical at

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the industrial scale. Other methods include high pressure homogenizers,[2] static mixers,[8] or rotor-stator mixers.[8,9] All of these devices are of interest at the current time since they have been widely used in other areas of agri- and petrochemical processes. It is clear that they can be economically viable, safely used and can be extrapolated for use on a large scale (not the case with ultrasound).

Earlier studies from other groups have shown that high pressure homogenisers are a credible alternative to ultrasound for the generation of dispersions,[2] thus we will not pursue this farther here, but rather will explore other alternatives to this route. Recent work by Ouzineb et al. investigated the use of the rotor-stator mixer, as well as in-line mixers to make miniemulsion droplets (300–800 nm) using styrene or butyl methacrylate as monomers with a solid content of 47.5%, sodium dodecyl sulphate (SDS) and Triton 405-X as emulsifiers, and stearyl methacryate (SMA) as a reactive co-stabiliser.[8] This work focused on different single monomer systems with similar levels of hydrophobicity, however the authors did not discuss polymerisations but focused only on the creation of the dispersions. In previous studies, Cunningham et al. used a high shear rotor-stator for the creation of microsuspension droplets (2–400 microns) of MMA containing AIBN, BPO and LPO as initiators and PVOH as the stabilising system.[9] Experimental methods consisted of mixing the pre-emulsified mixture for 4 minutes at 5000 rpm to make droplets of 10 μm, and 2 minutes at 15 000 rpm to make droplets of 2 μm. However these droplets are too small to be of practical use in the applications (e.g. coatings) that we are looking at here. The objective of the current paper is to present preliminary results obtained during the investigation of the use of a rotor-stator mixer for the production of mixtures of monomers with different hydrophocities (MMA plus BA), and to attempt to understand the role of the different process parameters in the evolution of the PSD during the reaction. Parallel work is being carried out on static mixers as a means of generating miniemulsions. A future paper from this research group will show these results and compare the different means of making miniemulsions.

Experimental Part

All compounds used in this study were used as received from the suppliers. The monomers were methyl methacrylate (MMA) and butyl acrylate (BA) were used as received. The surfactant used was sodium dodecylbenzene sulfate (SDBS) (Acros 88% technical grade) and Disponil® A 3065 (Cognis – 37%). The co-stabilisers tested were octadecyl acrylate (ODA) (Aldrich, 97%) and n-hexadecane (HD) (Acros, 99%). The oil soluble initiators used were dilauryl peroxide (LPO) (Acros, 99%), dibenzoyl peroxide (BPO) (Acros, 75%), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (Acros, 98%).

Miniemulsions were made using a 50:50 w/w mixtures of the two monomers with solid contents ranging from 47–55% weight percent. The organic phase contained 10 wt% co-stabiliser, 0.4–1.2 wt% of surfactant, and 0.14 wt% of initiator based on total monomer mass. Prior to emulsification, the monomers, co-stablisers and (eventually) oil soluble initiators were mixed together under gentle agitation at room temperature, and the surfactants were dissolved in the deionised water and prepared as a second phase. The two phases were then combined and subjected to high shear using the rotor – stator mixer. The miniemulsion droplets were made using a Turbotest® rotor - stator (RAYNERI) having a maximal rotation rate of 3300 rpm. The rotor stator assembly was a H30 Form B and a 5.5 cm interior diameter stator was used with a four blade rotor. The stator head has 19 vertical slits along the side and 12 circular slots along the top. The solutions to be emulsified were introduced into a 1 litre jacketed glass reactor containing a hexagonal baffle-like insert to reduce the vortex. This configuration was preferable to standard baffle configurations since the lack of sharp angles reduced opportunities for fouling and destabilisation of the mixture. All miniemulsions were stable without agitation for up to six hours. None of the emulsified solutions showed phase separation within two weeks of visual examination.

The polymerisations were carried out in a 2 L glass unbaffled reactor equipped with a reflux condenser, a nitrogen inlet, an anchor stirrer, and a sampling device. Initially the homogenised mixture was purged with nitrogen for approximately 25 minutes to remove any dissolved oxygen. All polymerisations were carried out with a constant jacket temperature of 70 °C. An anchor impeller set at 300 rpm was used to stir the reacting mixture. Once the polymerisation began (t = 0 minutes), samples were taken every 10 minutes for the first half an hour and then every half hour from there on.

Average droplet and particle sizes and size distributions were measured by Static Light Scattering using a Beckman-Coulter Counter LS-230. Full droplet and particle size distributions included number average (D_N) and volume average (D_V) values. Conversion was measured gravimetrically. Conductivity of the solutions was monitored with a Copenhagen CDM 83 conductivity meter equipped with platinum cells.

Results and Discussion

In an initial phase, we ran a series of emulsifications with different quantities of SDBS to identify a practical set of operating conditions using AIBN as the initiator and ODA as the co-stabiliser. The results, shown in Table 1, indicate that the rotor stator can be used to generate droplets of different sizes. It can be seen from this table that as the rotational speed is dropped, and as the surfactant concentration decreases one can make miniemulsions with larger and larger average particle sizes. Note that as the average particle size increases it becomes more and more challenging to maintain a narrow PSD. The width of the PSD is indicated by the ratio of D_v/D_N, the ratio of the volume average to the number average particle diameter. Ideally this would be unity for a perfectly monodispersed system, but anything less than 2 can be considered acceptable.

While this does not appear to have implications in the stability of the dispersed minemulsion droplets (as mentioned above, the miniemulsions appear to be stable for several hours – this means that the PSD did not evolve during the time considered – which is more than likely sufficient for industrial production) it might pose a problem for the polymerisation of the droplets. It would probably be more difficult to obtain a one-to-one mapping of droplets into polymer particles with miniemulsions with large PDIs (i.e. wide PSDs) because there can be some droplets for which the Laplace pressure is greater than the osmotic pressure, and others where the opposite is true. Discussion of this last point is beyond the scope of the current text, but will figure in a forthcoming publication from this group. In the rest of this paper we will focus on the influence of the different

Table 1.
Evolution of the droplet size (D_v) as a function of increased surfactant and rotational speed.

Name	Speed (rpm)	Time (min)	Surfactant* Conc. (wt %)	PDI (D_v/D_N)	D_v (nm)
R1	3000	95	1.2	2.6	311
R2	3000	90	0.8	1.2	399
R3	3000	80	0.8	1.4	514
R4	2500	75	0.64	1.5	595
R5	2500	65	0.48	1.7	694
R6	2500	50	0.4	2.0	1100
R7	2000	45	0.4	1.9	1960

* Weight percent with respect to total monomer mass (M_{TOT} = 250 grams).

process parameters on miniemulsions made with rotor stator mixers and the resulting polymeric dispersions using the conditions in R2 as a reference.

Role of Initiators

Droplets of ~400 nm in diameter were made using recipe R2 (50/50 w/w ratio of MMA:BA, 10 wt% ODA, and 0.8 wt% SDBS). Three different initiators (AIBN, LPO and BPO) were used in order to compare their conversion profiles.

The conversion profiles for the polymerisations initiated by AIBN, BPO and LPO are shown in Figure 1. It can be seen that the polymerisation initiated with AIBN polymerised faster than with LPO or BPO. This most likely due to the higher solubility of AIBN's in the water phase (4 g/L for AIBN vs. 3×10^{-3} and 2×10^{-8} g/L for BPO and LPO respectively[15]), which in turn contributed to secondary nucleation. This idea is supported by an increase in particle size diameter measured by volume but a decrease in the particle diameter by number (Table 2), thus causing the polydispersity index to increase dramatically (1.2 to 5.0). The increase in droplet diameter by volume could indicate that larger droplets are slowly coalescing due to a drop in the available surfactant caused by the increase in particle surface area due to the renucleated particles.

The polymerisation of miniemulsions with LPO and BPO as organo-soluble initiators (and incidently hydrophobes) showed similar results with respect to conversion, droplet diameter and polydispersity index (c.f. Table 2). With both initiators, the droplet diameter by volume and by number increased indicating that there is a certain amount of droplet coalescence occruing during the reaction. If new particles were formed by secondary nucleation in these runs, clearly they were not stabilised. The observations made in the above systems support prior observations made by Alduncin et al.[6] who performed work on simple styrene miniemulsion polymerisations and evaluated the use of the same three. They found that initiation in the water phase is expected when AIBN is used resulting in other forms of nucleation, but is expected to be less pronounced

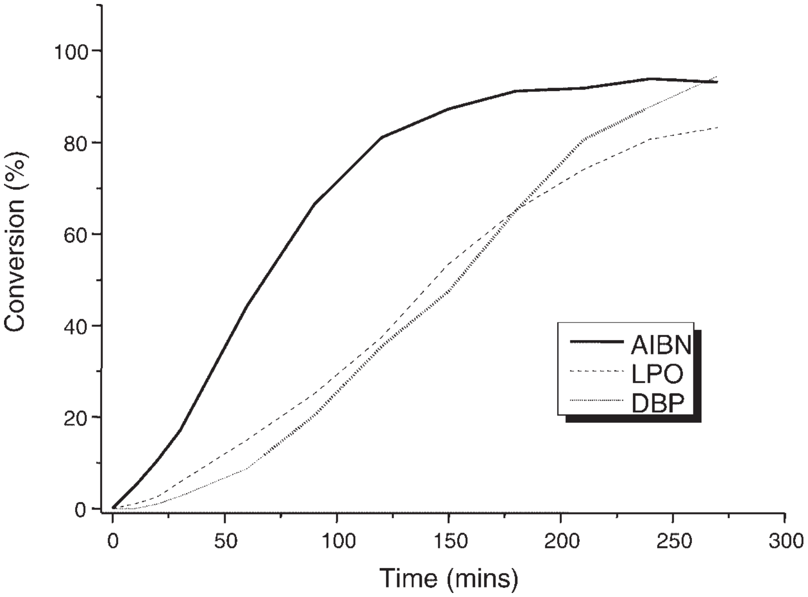

Figure 1.
Evolution of conversion over time as a function of the initiator used (AIBN, LPO and BPO) for ~400 nm droplets (R2) polymerised at 70 °C.

Table 2.
Evolution of the polydispersity index, conversion and droplet diameters by volume and number for ~400 nm droplets (R2) polymerised using AIBN, BPO and LPO at 70 °C.

Time (min)	AIBN				BPO				LPO			
	Dv (nm)	Dn (nm)	PDI	Conv (%)	Dv (nm)	Dn (nm)	PDI	Conv (%)	Dv (nm)	Dn (nm)	PDI	Conv (%)
0	402	313	1.3	0.0	392	294	1.3	0.0	410	321	1.3	0.0
10	426	336	1.3	4.9	400	286	1.4	1.6	418	337	1.2	1.2
20	432	278	1.6	10.6	392	294	1.3	10.4	420	321	1.3	2.6
30	462	118	3.9	16.9	411	315	1.3	16.7	474	319	1.5	5.8
60	505	127	4.0	44.3	412	300	1.3	25.4	478	337	1.4	15.0
90	484	107	4.5	66.5	438	327	1.3	32.3	559	331	1.7	25.1
120	545	118	4.6	81.1	511	297	1.7	49.4	618	331	1.9	37.5
150	547	122	4.5	87.3	502	294	1.7	60.6	622	354	1.8	53.5
180	542	132	4.1	91.2	555	308	1.8	70.8	693	353	2.0	65.2
210	543	116	4.7	91.9	582	321	1.8	75.9	740	370	2.0	74.1
240	587	128	4.6	93.4	584	352	1.7	80.6	656	340	1.9	80.7
270	555	111	5.0	93.2	658	359	1.8	83.4	747	372	2.0	83.3

with BPO and almost negligible with LPO. In our case, water phase nucleation is negligible for both BPO and LPO. Capek et al.[10] stated the LPO radicals are highly water insoluble and therefore reside on the inner surface of the particle, as such they will act as hydrophobes as pointed out by Alduncin et al.[6] However, Table 2 also shows that even in the presence of a dedicated hydrophobe, the water solubility of the AIBN initiated radicals contributes to the destabilisation of the system via a mechanism of secondary nucleation.

Role of Co-stabiliser

For all polymerisations presented in this work, ODA was used as the (polymerisable) co-stabiliser. ODA has a low molecular weight (MW 324.54 g/mol) and very low water solubility. ODA is also a monomer which means there is a possibility for it to react during the polymerisation. The role of co-stabiliser is crucial in miniemulsion droplets as it prevents or delays the rate of Ostwald ripening. To understand the eventual effect that the polymerisation of ODA had on our particles, runs were run where ODA was replaced with hexadecane (HD), keeping all other components the same. Hexadecane is obviously not consumed during the polymerisation. Figure 2 below shows the evolution of particle sizes over time as a function of the co-stabiliser used. Based on the evolution of the droplet/particle size it can be seen that changing the co-stabiliser has little observable influence on the course of the reaction. This is not surprising since ODA is consumed relatively slowly during the reaction, and is progressively replaced with polymer which also acts as a hydrophobe.

Role of Solid Content

Although high solid content systems are desirable, the likelihood of particle-particle interaction is enhanced possibly leading to the coalescence of particles if their surfaces are not well stabilised. The systems prepared in our work consisted of ≥45 wt % solid content depending on the desired droplet size. In the case of ~400 nm droplets, the solid content was 47 wt %. As seen previously at this solid content, we observed an increase in particle size during polymerisation from ~400 nm to ~700 nm (Figure 3(A)). Conductivity measurements, which reflect the amount of free anionic surfactant in solution, showed that as particle size increased, the amount of surfactant desorbed from the particle surface also increased (Figure 3(B)) (see Reimers and Schork[11]). Hence, to evaluate the influence of high solid content on the rate of flocculation of the particles we ran a similar system but with a reduced solid content (34 wt %) keeping the wt % of the co-stabiliser and surfactant constant relative to monomer mass.

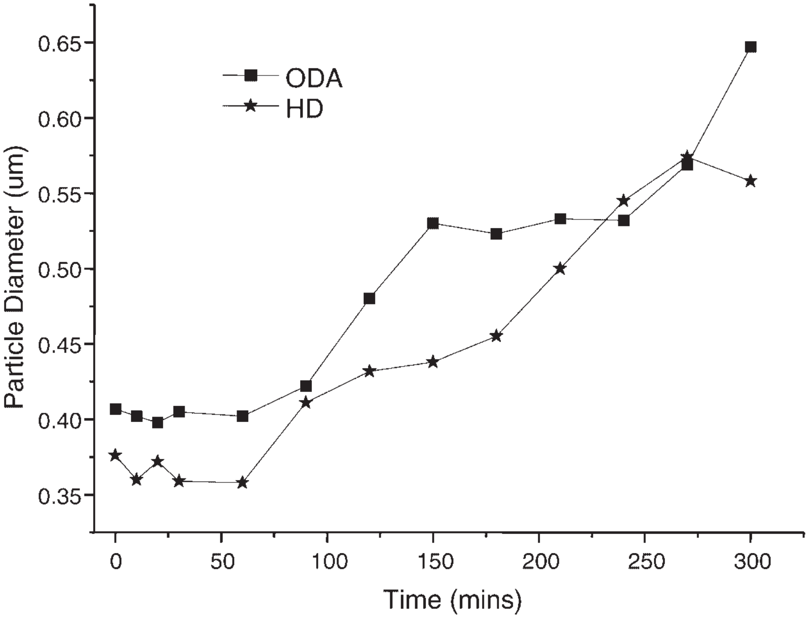

Figure 2.
Evolution of the particle diameter (D_v) over time as a function of the co-stabilisers ODA and HD for ~400 nm droplets polymerised at 70 °C using BPO.

As it can be seen from Figure 3, irrespective of the solid content, the particle size remained similar and continued to increase throughout the polymerisation. Conductivity measurements (Figure 3(B)) also increased in similar magnitudes over time. Exactly why this is occurring is not clear, and further work needs to be done to clarify this point. Nevertheless, it is clear that this type of behaviour could lead to an accumulation of surfactant in the water phase during later stages of the reaction, and thus create conditions conducive to the renucleation of particles. This might help to explain the results seen with AIBN above.

Surface Coverage

In the experiments presented above, the particle size continued to increase as the reaction progressed, undoubtedly because the internal nature of the particles evolves as the relative quantities of monomer, polymer and hydrophobe change due to polymerisation. We therefore decided to take a closer look at the actual surface coverage of the droplets by taking conductivity measurements. Initially, the evolution of conductivity as a function of the volume of added anionic surfactant (SDBS) solution was measured by slowly adding SDBS at a constant flow rate to a volume of water. From Figure 4 it can be seen that there is a change in the slope at a volume of 1.7 mL, indicating a CMC value of approximately 0.83 g/L. Conductivity measurements of our aqueous phase prior to emulsification indicate that we are above the CMC (1.86 mS/cm).

Conductivity measurements were also taken after the two phases were emulsified and we achieved ~400 nm droplets (1.25 mS/cm). Based on conductivity measurements our emulsified solution already contains micelles. We theoretically have a surface coverage of 33% based on calculations using Equation (1):

$$\% \text{ Coverage} = \left(\frac{m_{SDBS}}{M_{SDBS}} \times A_s \times N_A\right) \times \left(\frac{M_{pol}}{d_{pol}} \Big/ \frac{\pi}{6} \times D_p\right)^{-1} \tag{1}$$

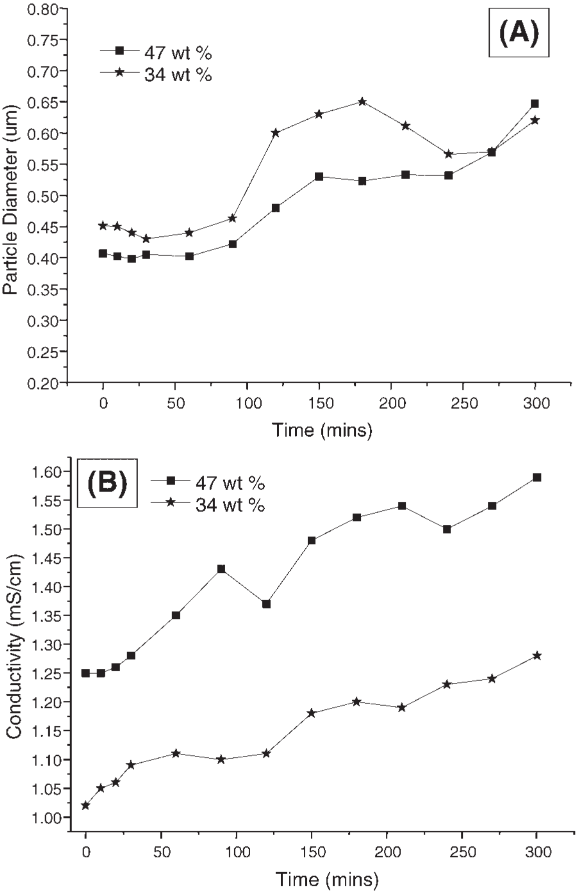

Figure 3.

Evolution of the particle diameter (Dv) with time as a function of the solid contents 47 and 34 wt% (A, top) and evolution of the conductivity (mS/cm) over time as a function of the solid contents 47 and 34 wt% (B, bottom) for ~400 nm droplets polymerised at 70 °C using BPO.

Here, m_{SDBS} is the mass of SBDS used, M_{SDBS} is the molecular weight of SDBS, A_s is surface area per molecule of SDBS, N_A is Avogadro's number, M_{pol} is the mass of polymer, d_{pol} is the density of the polymer and D_p is the diameter of the particle. Upon polymerisation, the particles continue to increase in size and the surfactant is subsequently released into the water phase. Further calculations showed that of the entire amount of surfactant that was put through emulsification, only 41% was actually located at the oil-water interface. The evolution of the surface coverage during the reaction is shown in Table 3. Here it can be seen that, for the experiment in question, initially 41% of the surfactant is located at the oil – water interface, but as the polymerisation progresses it drops to approximately 18% after 5 hours.

If we increase the theoretical initial surface coverage to approximately 60% (i.e. the quantity of surfactant is doubled to 1.6% w.r.t. monomer), we are again above the CMC both before and after emulsification, and during the polymerisation. As shown in Table 4, the conductivity increases once again during the reaction, and although the final surface coverage is approximately 38% a certain amount of coalescence is once again observed and we end up with particles with diameters of 620 nm. Similarly, if one

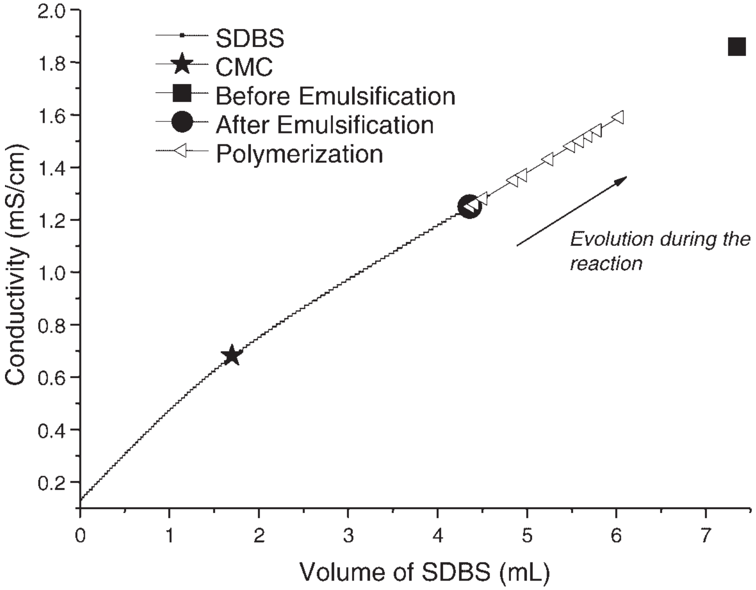

Figure 4.
(--) Evolution of the conductivity as a function of the volume of SDBS added to a volume of DIW, the aqueous phase prior to emulsification, the emulsified mixture, and the misture during the polymerisation for droplets prepared with a theoretical surface coverage of 30%.

Table 3.
Evolution of the conductivity as a function of the particle diameter throughout the polymerisation and the percentage of surfactant that is located at the oil – water interface for droplets made with a theoretical surface coverage of 30%.

Time (min)	Conductivity (mS/cm)	D_V (nm)	% Surfactant at Interface
10	1.25	402	41
20	1.25	398	41
30	1.26	405	40
60	1.28	402	39
90	1.35	422	34
120	1.43	480	29
150	1.37	530	33
180	1.48	523	25
210	1.52	533	22
240	1.54	532	21
270	1.50	569	24
300	1.54	530	18

Table 4.
Evolution of the conductivity as a function of the particle diameter throughout the polymerisation and the percentage of surfactant that is located at the oil – water interface for droplets made with a theoretical surface coverage of 60%.

Time (mins)	Conductivity (mS/cm)	D_v (nm)	% Surfactant at Interface
10	1.97	388	49
30	2.01	400	47
90	2.06	376	46
120	2.10	411	45
240	2.19	654	41
300	2.29	620	38

triples the amount of surfactant, the final particle size is similar (585 nm).

Conclusions

The application of the rotor stator to develop miniemulsion droplets was examined. It was found that it is possible to produce droplets ranging from 300 nm up to 2 μm at industrially pertinent solid contents. It was shown that by increasing rotational speed and surfactant quantity we were able to decrease the droplet size. Although the rotor stator does require more time to generate these droplets than, for example, ultrasonication, the major advantage is that it can be applied to large batches.

The droplets generated with the rotor stator were polymerised to evaluate particle diameter evolution. It was found that droplets on the order of 300–400 nm increased in size during polymerisation. After examining different parameters such as changing the co-stabiliser, decreasing the solid content, adding colloidal protectors and increasing surface coverage we were not able to directly show the cause for the particle size growth. The most likely explanation is that as the droplets are evolving into particles, the hydrophobicity of the particles increases as MMA is consumed and as polymer is produced. The initial stabilisation system on the droplets that kept the droplets stable for hours is no longer sufficient to define the evolving particles, causing them to coagulate. More work needs to be done on these points, and the results of this on-going study will be discussed in a future paper.

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