Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Oil droplet size manipulation applied to surfactant-free emulsion polymerization

M.J. Francis^{a,*}, T.K. Boyson^a, R.M. Pashley^b^a Department of Chemistry, The Faculties, The Australian National University, Canberra, ACT 0200, Australia^b Division of Research and Development, Murdoch University, Perth, Australia

ARTICLE INFO

Article history:

Received 7 November 2007

Received in revised form 5 May 2008

Accepted 11 June 2008

Available online 19 June 2008

Keywords:

Emulsion polymerization

Particle size manipulation

Degassed emulsions

ABSTRACT

Recently reported results indicate that heating of degassed oil in water emulsions reduces the size of the droplets and can produce a more mono-disperse dispersion, in the absence of surfactants. In this work, these results were applied to the field of emulsion polymerization, to create meta-stable, mono-disperse monomer solutions, which were then polymerized to produce stable dispersions of polymer spheres. The product particle size depended on a range of factors, including: salt concentration, type of thermal initiator, temperature changes, creaming time, pH and monomer/initiator concentration ratio.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Latex paints are now the most popular type of paint for coating surfaces because water is used for dispersing the latex spheres, which coalesce to make the film, as opposed to the harsh organic solvents which would be required to dissolve the coating polymer [1]. Emulsion polymerization is carried out in the absence of oxygen and usually in high concentrations of surfactant (typically, 1:25 surfactant to monomer ratio) [1]. In 2003, it was discovered that the almost complete removal of dissolved gas from a mixture of oil and water allowed a meta-stable, dilute emulsion to be formed, upon vigorous shaking, without the need for surfactants [2]. In earlier work, partial degassing was found to change the latex particle morphology produced by the surfactant-free emulsion polymerization of styrene [3]. The almost complete removal of all dissolved gases will allow the polymerization reaction to take place in an oxygen-free atmosphere and the degassing of the monomer/water emulsion will facilitate the dispersion of monomer droplets, without the need for high concentrations of surfactants. This degassing dispersion process was also recently successfully applied to the emulsion polymerization of styrene, mediated using the reversible addition-fragmentation chain transfer (RAFT) process [4]. Degassing allowed for the omission of surfactants, which would otherwise offer com-

peting micelle nucleation centres. The RAFT process is used to control average polymer molecular weight and the size distribution.

A further benefit of completely removing the surfactants is that the polymer spheres formed without surfactant will have unadulterated surfaces, which should coalesce more readily during film drying. This is partly because of the higher interfacial tension expected for the latex particle/water interface, which will give an extra driving force for film formation. Also, inter-particle penetration between polymer segments will be less hindered because of the removal of the surfactant coating.

In 2007, it was discovered that heating of degassed emulsions reduced the size of the droplets creating a new meta-stable solution, often with a narrower size distribution [5]. It was discovered in a follow up study that both the pH and the ratio of oil to water also affected the particle size of the droplets [6]. In this current work, we have studied the dispersion properties of polymerizable oil, 4-fluorostyrene, under degassed conditions and under a variety of conditions which altered the droplet sizes. This oil was also chosen because it has a density (1021 kg/m³) close to that of water, which means that fine droplets will not readily phase separate in water. It has already been established that oil droplets do not coalesce, once formed under degassed conditions [7]. The meta-stable oil droplets were then thermally polymerized, over several hours, to produce a latex dispersion. The polymer particle sizes were determined by SEM and dynamic light scattering. The average molecular weight of the polymers produced was also determined.

* Corresponding author.

E-mail address: mathew.francis@anu.edu.au (M.J. Francis).

Fig. 1. Particle size distribution for a degassed 1:500 parafluorostyrene monomer/water emulsion with no initiator added, measured at 60 °C using DLS. The peak diameter was found to be 2800 nm, the Z-average 2440 nm and the PDI 0.179.

Fig. 2. Particle size distribution for a degassed 1:500 parafluorostyrene monomer/water emulsion with 1% AIBN by weight, measured at 60 °C. Peak diameter 3480 nm, Z-average 2990 nm and PDI: 0.063.

Fig. 3. Particle size distribution for a degassed 1:125 poly(parafluorostyrene)/water emulsion. The monomer was polymerized for 9 h at 60 °C with 1% AIBN initiator by weight. Particle size was measured at 25 °C using DLS. The peak diameter was found to be 630 nm, Z-average 528 nm and the PDI: 0.157.

Fig. 4. Particle size distribution for a degassed 1:125 poly(parafluorostyrene) emulsion. The monomer was polymerized for 9 h at 60 °C with 1% sodium persulfate initiator. The particle size was measured at 25 °C. The peak diameter was found to be 360 nm, the Z-average 279 nm and the PDI: 0.234.

Fig. 5. Comparison of the particle size distributions obtained with degassed 1:125 poly(parafluorostyrene)/water emulsions, polymerized with either 1% persulfate or 1% AIBN, measured at 25 °C.

Fig. 6. Chloroform solution viscosities of degassed 1% persulfate and 1% AIBN initiated poly(4-fluorostyrene). The lines were extrapolated to the y-axis to determine the intrinsic viscosity for each initiator.

2. Materials and methods

Water was prepared by activated charcoal and reverse osmosis filtration prior to distillation and storage in Pyrex vessels in a laminar flow filtered air cabinet. The monomers used here were: 4-fluorostyrene, methylmethacrylate and perfluorostyrene. The thermal, radical initiators were: potassium persulfate and azobisisobutyronitrile (AIBN). All were used as purchased, typically at >99% purity. The monomer/water mixtures, with added initiator (usually 1% by weight), were degassed over 4–5 freeze-pump-thaw cycles. They were then shaken for 30 s at room temperature and then allowed to equilibrate for 20–30 min, to allow gravity separation of any large droplets, produced during shaking. The sealed, degassed sample tubes were then placed into a water bath at 60 °C for about 9–10 h. The tubes were then removed from the bath and allowed to cool to room temperature and droplet size measurements were then obtained with a Nano ZS zetasizer at 25 °C. Upon polymerization the monomer emulsions became much more turbid, indicating that there were more droplets but of smaller size after polymerization. There should have been no significant loss of monomer from the sealed tubes during heating because of the high boiling point of 4-fluorostyrene of about 150 °C. For long-term stability tests, the latex solutions were stored in sealed glass tubes under gassed conditions.

Degassed poly(4-fluorostyrene) solutions, initiated with either AIBN or persulfate, were dried under vacuum leaving a solid white

powder. The resulting solid was then dissolved in chloroform. The molecular masses of these polymer samples were determined from the viscosities of a series of chloroform solutions, measured using an Ubbelohde viscometer, at 25 °C. SEM samples were prepared by air drying polymer dispersions, initiated by persulfate or AIBN, directly on SEM stubs. The dried samples were then vacuum-coated with a fine layer of gold prior to imaging. The SEM images were taken using a Hitachi S-4300 SE/N Scanning Electron Microscope.

3. Results

Pure, liquid 4-fluorostyrene monomer, with 1% AIBN initiator added, was found to polymerize in bulk, even in the presence of dissolved oxygen, at a temperature of 60 °C, over several hours, producing a solid block of polymer. Initial experiments confirmed that the oil 4-fluorostyrene, with no added initiator, could be readily dispersed in water using the degassing technique. The emulsion produced, at an oil/water ratio of 1:500, gave a size distribution with a Z-average (or number average) droplet diameter of 16,800 nm and a PDI of 0.185, at 25 °C. Upon heating this emulsion to 60 °C (Fig. 1) the Z-average dropped by a factor of 8 and the mixture formed a sharper size distribution. AIBN initiator (1%) was added to the monomer and the experiment repeated. Prior to heating, the Z-average size was 20,300 nm and the PDI was 0.333. Upon heating the solution, the particle size and PDI were substantially reduced, as shown in Fig. 2.

Fig. 7. SEM photograph of 1:12,500 AIBN initiated poly(4-fluorostyrene)/water emulsion air dried onto an SEM stub. The observed particles were spherical with an approximate diameter of 400 nm.

A 1:500, 4-fluorostyrene in water emulsion, dispersed by shaking following degassing, was then polymerized by heating to 60 °C for 9 h, to ensure as much of the monomer as possible was converted to polymer. Figs. 3 and 4 show distributions of 4-fluorostyrene emulsions polymerized for 9 h, using AIBN and potassium persulfate, as initiators. These results show that both initiators produced a substantial reduction in particle size but the persulfate initiator produced the smallest particle size. Fig. 5 shows a comparison between the particle size distribution of the heated monomer dispersion, prior to polymerization, and the polymerized dispersions obtained using the two different initiators. The reduction in size is clearly demonstrated. This may in part be due to the formation of larger numbers of smaller particles, which also causes the solution to become much cloudier with an appearance similar to that of milk. It may also be that excess monomer was solubilized into the aqueous phase and so was not significantly polymerized during heating.

The molecular masses (M in g/mole) of the poly(4-fluorostyrene) polymer prepared using persulfate and AIBN initiator were determined using the Mark-Houwink (M-H) viscosity method. The M-H constants for the poly(4-fluorostyrene) system in chloroform at 25 °C are $K = 0.0161$ (ml/g) and $\alpha = 0.69$ [8]. Fig. 6 shows the graphs of the specific viscosity divided by the concentration versus the concentration. The y-intercept gives the intrinsic viscosity $[\eta]$. Using the M-H equation: $[\eta] = KM^\alpha$, the molecular mass of AIBN initiated poly(4-fluorostyrene) was estimated to be about 168,000 g/mole, while for persulfate initiated poly(4-fluorostyrene) the molecular mass was estimated to be about 143,000 g/mole.

Figs. 7 and 8 show typical SEM photos of the latex particles formed using the two initiator systems. These observations also confirm the slightly lower size of the persulfate initiated polymer particles. Fig. 7 shows the AIBN polymer spheres are about 400 nm in diameter while Fig. 8 indicates that the persulfate initiated poly(4-fluorostyrene) spheres were about 250 nm in diameter.

The particle size distribution of two more polymerized particles, poly(methylmethacrylate) and poly(perfluorostyrene) were also measured, again using two different initiators for each monomer. Fig. 9 shows the size distribution for 1:125 methyl methacrylate/water with AIBN initiator. The persulfate initiated dispersion using methylmethacrylate was found to be polydisperse, with a wide range of sizes, suggesting that the polymerization occurred

Fig. 8. SEM photo of degassed 1:12,500 persulfate initiated poly(4-fluorostyrene)/water emulsion air dried onto an SEM stub. The particles observed were spherical with a diameter of about 250 nm.

more rapidly, before the larger monomer droplets were settled out. Figs. 10 and 11 show perfluorostyrene latexes polymerized with persulfate and AIBN, respectively. Fig. 12 shows the comparison between the two different size distributions obtained with different thermal initiators for the perfluorostyrene system. Again the data shows that the persulfate initiated polymer spheres were smaller than those initiated by AIBN. A summary of these results for the different monomer and thermal initiator systems is given in Table 1.

In a final series of experiments, the effect of increasing the polymerization temperature to 70 °C was studied. Fig. 13 shows that the particle sizes of poly(4-fluorostyrene) could be further reduced, with a narrower distribution, at higher temperatures. The effect of longer settling times (at 25 °C), prior to emulsion polymerization, is illustrated in the results presented in Fig. 14.

Another method used earlier to alter dispersion size in tandem with heat clarification, was to alter the pH. It was found in earlier work [9] that controlling the amount of hydroxyl ions in solution directly influenced the size of the oil droplets produced during the degassing dispersion process. This is because adsorbed hydroxyl ions stabilize the oil droplets and prevent their coalescence. The effect of pH on the final particle size of poly(4-fluorostyrene) dispersions is shown in Fig. 15. From the graph we can see that the emulsions measured at pH 7 and 10 have a similar particle size while the emulsion measured at pH 3 has a much larger particle size.

The effect of increasing the concentration of the 4-fluorostyrene monomer by a factor of five times was also studied. The effect on the particle size distribution is shown in Fig. 16. At the higher monomer levels, the latex particles were found to be substantially larger. Lastly, the long-term stability of the polymer solutions was tested. A solution of 1:125 poly(4-fluorostyrene) in water, which had been polymerized with AIBN, was left in a sealed glass tube

Table 1

A comparison of average particle sizes and size distributions for several different monomer and initiator mixtures

Monomer + initiator	Z-average (nm)	Peak diameter (nm)	PDI
4-Fluorostyrene + AIBN	528	630	0.157
4-Fluorostyrene + persulfate	279	360	0.234
Perfluorostyrene + AIBN	412	436	0.053
Perfluorostyrene + persulfate	241	224	0.265
Methylmethacrylate + AIBN	3230	3440	0.065

Fig. 9. Particle size distribution for a degassed 1:125 poly(methyl methacrylate)/water emulsion. The monomer was polymerized with AIBN initiator for 9 h at 60 °C. The particle size was measured using DLS at 25 °C. The peak diameter obtained was 3440 nm, Z-average 3230 nm and the PDI: 0.065.

Fig. 10. Particle size distribution for a degassed 1:125 poly(perfluorostyrene)/water emulsion. The monomer was polymerized with sodium persulfate initiator for 9 h at 60 °C. The particle size was measured at 25 °C. The peak diameter was found to be 224 nm, the Z-average 241 nm and the PDI: 0.265.

and the particle size distribution was re-measured 1 month later. A comparison of three measurements of the particle size, each 1 month apart is shown in Fig. 17.

4. Discussion

This study has demonstrated that heating degassed-dispersed, surfactant-free, emulsions can be used to reduce their average droplet size. Also, using a polymerizable monomer, such as 4-fluorostyrene, the resulting polymer latex produced by radical, thermal polymerization, shows still further reductions in average size. As an example, AIBN, an organic phase thermal initiator, produced a narrow distribution of spherical latex particles, with

a peak diameter of 630 nm, which agreed reasonably well with the Z-average value of 528 nm. The PDI of this dispersion was found to be 0.157. By comparison, the Z-average of the initial room temperature dispersion was much larger, in the range of about 17,000–20,000 nm.

In an effort to reduce the size of the polymer spheres still further, an aqueous phase initiator was used, potassium persulfate. Using this initiator, the dispersion produced gave a lower peak diameter of 360 nm, with a Z-average of 279 nm and a PDI of 0.234. The persulfate initiated samples produced a smaller average particle size, possibly due to an increased electrostatic stabilization of the particles, due to the presence of additional charged $-\text{SO}_4^-$ groups on the particle's surface. This difference in

Fig. 11. Particle size distribution for a degassed 1:125 poly(perfluorostyrene)/water emulsion. The monomer was polymerized with AIBN initiator for 9 h at 60 °C. The particle sizes were measured at 25 °C. The peak diameter was found to be 436 nm, the Z-average 412 nm and the PDI: 0.053.

Fig. 12. Comparison of the particle size distributions of degassed 1:125 poly(perfluorostyrene)/water emulsions polymerized with either 1% persulfate or 1% AIBN, measured at 25 °C.

Fig. 13. Comparison of the particle size distributions for degassed 1:125 poly(parafluorostyrene)/water emulsions initiated with AIBN at 60 and 70 °C.

Fig. 14. Comparison of particle size distributions for degassed 1:125 poly(perfluorostyrene)/water emulsions initiated with AIBN polymerized immediately and polymerized after a 5 h delay after dispersion.

Fig. 15. Particle size comparisons of degassed 1:125 poly(parafluorostyrene)/water emulsions initiated with AIBN at pH 3, 7 and 10. At pH 3 the peak diameter was found to be 1870 nm, the Z-average 1900 nm and the PDI was 0.299. At pH 7 the peak diameter was found to be 597 nm, the Z-average 504 nm and the PDI 0.196. At pH 10 the peak diameter was 387 nm, the Z-average 342 nm and the PDI 0.243.

Fig. 16. Comparison of the particle size distributions of degassed 1:125 poly(parafluorostyrene)/water and 1:25 poly(parafluorostyrene)/water emulsions initiated with AIBN and polymerized for 9 h.

Fig. 17. Comparison of the particle size distribution of degassed 1:125 poly(parafluorostyrene)/water emulsion initiated with AIBN for 9 h, then measured over several months at 25 °C.

size between the two initiators was also confirmed by SEM studies.

Another interesting aspect of these degassed polymer emulsions was their ability to form films on drying. Most commercial latex polymers are used at a polymer/water ratio of 1:1, however, they also have a high level of surfactant, which hinders film formation. Fig. 18 shows an SEM of a film formed by a dilute latex solution formed using the degassing dispersion technique, followed by ther-

mal polymerization. The dilute dispersion had a polymer/water ratio of only 1:12,500. The polymer was initiated with persulfate using dispersed 4-fluorostyrene oil as the monomer. The film was cracked, probably due to the low concentration of polymer and individual latex particles are observed on the surface of the film. These particles must have settled onto the film late in the drying process, after the film had formed.

Two other monomers were also tested and gave similar results. AIBN initiated poly(perfluorostyrene) had a peak average diameter of 436 nm, a Z-average of 412 nm and a PDI of 0.053, while the persulfate initiated poly(perfluorostyrene) had a peak average diameter of 224 nm, a Z-average of 241 nm and a PDI of 0.265. These results again confirm a halving of the diameter of the polymer spheres when persulfate initiator is used in preference to AIBN. Methylmethacrylate was also successfully dispersed in solution using the degassing technique. The poly(methylmethacrylate) dispersion had a much larger peak diameter of 3440 nm, a Z-average 3230 nm and a PDI of 0.065, showing that this monomer in tandem with AIBN creates a narrow distributed solution of polymer spheres. By comparison, persulfate initiated methylmethacrylate samples were polydisperse, with spheres of widely divergent sizes created. This could have been due to the speed at which this monomer polymerized, with particles of all sizes polymerizing before the larger monomer spheres could settle out.

As the results in Table 1 demonstrate, the difference in particle size for the final latex spheres was dependent on the monomer, as well as the initiator. It is evident from these results that not only does persulfate halve the diameter of the spheres created but it also creates more polydisperse samples, probably due to the mechanism of the polymerization process. In all cases observed, persulfate ini-

Fig. 18. SEM photograph of the film formed when a droplet of degassed 1:12,500 poly(4-fluorostyrene)/water emulsion, sodium persulfate initiated, was air dried on an SEM stub.

tiated samples had a higher final PDI than AIBN samples. AIBN is an oil soluble monomer and will initiate polymerization within the droplets. Persulfate on the other hand is water soluble and will initiate in the water phase, with radicals reacting at very low concentration of monomer in the water phase. In the case of persulfate the radicals must grow to a certain chain length to become surface active and enter droplets. If there are too few droplets then secondary particles are formed by way of the radicals growing to a large size and collapsing into small secondary particles. This leads to the larger distribution seen for the persulfate initiated samples.

Increasing the polymerization temperature by ten degrees caused the final size of the spheres to be substantially reduced, from 528 to 324 nm, for the case of poly(parafluorostyrene), see Fig. 13. The effect of increasing settling times prior to emulsion polymerization had the opposite effect to that expected. Instead of the final average size getting smaller, as would be expected with more of the larger droplets settling out of the emulsion, the average size actually increased (see Fig. 14). This observation was most likely due to the coalescence of the finer droplets prior to polymerization. The initiator used for this series of experiments was AIBN. If some of the small droplets did not include initiator they would have time to bind with other droplets before polymerization, leading to the higher sizes.

The pH of the mixture prior to polymerization also changed the droplets size. Adding base dropped the final size slightly and adding acid increased the final size dramatically (see Fig. 15). That increasing the pH only had a slight effect on reducing the average size, was most likely due to the fact that the droplets were already close to complete surface coverage, for that given size at neutral pH 7. This conclusion was supported by the results observed when the pH was dropped to 3. In this case the diameter of the droplets increased by more than a factor of three, which is expected if the surface of the monomers are stripped of hydroxyls, allowing them to merge because of the reduced electrostatic repulsion, before polymerization.

Droplet size variations were also observed as the monomer concentration was increased. Increasing the concentration five times lead to the formation of much larger droplets (see Fig. 16). This was probably because there were more monomers per hydroxyl ion to stabilize, allowing larger droplets to form, as was seen when the

pH was dropped to 3. Stability tests were carried out on several polymer latex samples over a period of several months. The distributions of the polymer solutions remained largely unchanged, showing that these dispersions generally remain stable, indefinitely, and the solution can be regenerated by simply shaking the vessel.

5. Conclusion

The average size of monomer droplets, dispersed in water using the degassing technique, can be substantially reduced by heating. The size of these droplets can be further reduced by radical, thermal polymerization. The final size of the polymers prepared under degassed conditions can also be altered by changing initiator type, pH and salt concentration. All of which can be achieved without the use of any added surfactant. The resulting latex solutions are stable and can then be stored for a long period of time, with no change to the particle size.

References

- [1] R.M. Pashley, M.E. Karaman, *Applied Colloid and Surface Chemistry*, first ed., J. Wiley, London, 2004.
- [2] R.M. Pashley, Effect of degassing on the formation and stability of surfactant-free emulsions and fine teflon dispersions, *J. Phys. Chem. B* 107 (7) (2003) 1714–1720.
- [3] M.E. Karaman, B.W. Ninham, R.M. Pashley, Effects of dissolved gas on emulsions, emulsion polymerisation and surfactant aggregation, *J. Phys. Chem.* 100 (1996) 15503–15507.
- [4] J. Hartmann, C. Urbani, M.R. Whittaker, M.J. Monteiro, Effect of degassing on surfactant-free emulsion polymerizations of styrene mediated with RAFT, *Macromolecules* 39 (3) (2006) 904–907.
- [5] M.J. Francis, T.K. Boyson, R.M. Pashley, Changing the particle size of oil droplets dispersed in water without added surfactants, *Colloids Surf. A: Physicochem. Eng. Aspects* 316 (1–3) (2008) 136–141.
- [6] M.J. Francis, R.M. Pashley, Further studies into oil droplet size manipulation, *Colloids Surf. A: Physicochem. Eng. Aspects*, submitted for publication.
- [7] N. Maeda, K.J. Rosenberg, J.N. Israelachvili, R.M. Pashley, Further studies on the effect of degassing on the dispersion and stability of surfactant-free emulsions, *Langmuir* 20 (8) (2004) 3129–3137.
- [8] J. Brandrup, *Polymer Handbook*, 2, fourth ed., Wiley-Interscience, New York, 1999.
- [9] M.J. Francis, R.M. Pashley, The effect of de-gassing on the dispersion of fine oil droplets in water, *Colloids Surf. A: Physicochem. Eng. Aspects* 287 (1–3) (2006) 36–43.