

# Mixed Initiator Approach to the Surfactant-Free Semicontinuous Emulsion Polymerization of Large MMA/BA Particles

K. J. O'CALLAGHAN,<sup>1</sup> A. J. PAINE,<sup>2</sup> and A. RUDIN<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1, Canada; <sup>2</sup>Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, ON L5K 2L1, Canada

## SYNOPSIS

The emulsion polymerization of large monodisperse MMA/BA copolymer particles by surfactant-free means at high solids content is described. A series of sequential seeded growth reactions were used to obtain monodisperse particles with diameters of at least 3 microns. A combination of an oil-soluble initiator, AIBN, and a water-soluble initiator, ammonium persulfate (AP), was used. The AIBN initiated the bulk of the polymerization and the AP provided the stabilization for the polymer particles through its charged endgroups. The amount of AP initiator to be used in each growth step was calculated empirically using a criterion of a constant ratio of moles of sulfate groups to the polymer particle surface area.

© 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Monodisperse polymer particles with diameters in the 1–10 micron range have many applications in fields such as biology, medical analyses, protein synthesis, chromatography, and xerography. With today's environmental concerns, emulsion polymerization, with its aqueous continuous phase, is a particularly attractive method in which to synthesize these particles.

At these large particle sizes, there is an increased likelihood of emulsion polymer forming freshly nucleated secondary particles instead of adding to existing particles. This reflects the fact that a given mass concentration of polymer presents a smaller surface to the aqueous phase, where polymerization is initiated, with larger sizes. The amount of surfactant must be then carefully maintained in a range where it is high enough to prevent coalescence yet low enough to avoid forming secondary particles.

The addition of surfactant to the emulsion polymerization system is not always necessary due to the stabilizing effect of oligomers that contain initiator residues such as the anionic sulfate group from the

use of persulfate initiators. These so-called *in situ* surfactants enable one to perform polymerizations with only water, monomer, and initiator, provided that the emulsion concentration is not too high.

In surfactant-free reactions initiated by ionic initiators, reducing the amount of *in situ* surfactant without compromising the initiation level would be impossible. This limitation can be overcome by using a mixed initiator system where the ionic initiator provides the *in situ* surfactant and a nonionic initiator such as AIBN provides the majority of the initiation.

This article outlines a procedure for producing large monodisperse copolymer particles by surfactant-free seeded semicontinuous polymerization methods at 30% solids content. A mixed initiator combination was used whereby a water-soluble and an oil-soluble initiator are added simultaneously to a surfactant-free system. The amounts of the water-soluble initiator, ammonium persulfate, to be used are calculated empirically using the criterion of a constant ratio of moles of sulfate groups to polymer particle surface area.

## EXPERIMENTAL

### Chemicals

Methyl methacrylate (MMA), butyl acrylate (BA), and ammonium persulfate (AP) were obtained from

\* To whom correspondence should be addressed.

**Table I** Reaction Recipes (Amounts in Grams)

|             | Stage # |        |        |        |        |        |        |        |        |
|-------------|---------|--------|--------|--------|--------|--------|--------|--------|--------|
|             | 1       | 2      | 3      | 3      | 4      | 5      | 6      | 7      | 8      |
| Reaction    | X1-127  | X2-130 | X3-132 | X3-137 | X4-138 | X5-139 | X6-141 | X7-142 | X8-143 |
| Seed        | —       | X1-127 | X2-130 | X2-130 | X3-137 | X4-138 | X5-139 | X6-141 | X7-142 |
| Amount seed | —       | 100    | 150    | 150    | 150    | 200    | 300    | 450    | 630    |
| Water       | 350     | 350    | 350    | 310    | 310    | 330    | 330    | 330    | 335    |
| AP          | 1.00    | —      | —      | —      | —      | —      | —      | —      | —      |
| AIBN        | —       | 0.05   | 0.05   | 0.05   | 0.05   | 0.05   | 0.05   | 0.05   | 0.05   |
| MMA         | 95.55   | 95.55  | 95.55  | 95.55  | 95.55  | 95.55  | 95.55  | 95.55  | 95.55  |
| BA          | 54.45   | 54.45  | 54.45  | 54.45  | 54.45  | 54.45  | 54.45  | 54.45  | 54.45  |
| IOMP        | 0.75    | 0.75   | 0.75   | 0.75   | 0.75   | 0.75   | 0.75   | 0.75   | 0.75   |
| AIBN        | —       | 0.95   | 0.95   | 0.90   | 0.92   | 0.93   | 0.93   | 0.94   | 0.94   |
| AP          | —       | —      | —      | 0.051  | 0.030  | 0.022  | 0.013  | 0.010  | 0.008  |
| Water       | —       | —      | —      | 40     | 40     | 20     | 20     | 20     | 15     |

Aldrich. Azobisisobutyronitrile (AIBN) was obtained from Polysciences Inc. and isooctyl-3-mercaptopropionate (IOMP) was received from Evans Chemetics (W. R. Grace & Co.). These chemicals were used without further purification. All water was deionized.

### Synthesis of MMA/BA Latexes

The MMA/BA (63.7/36.3 by wt) copolymer particles were made at 30% solids level by semicontinuous emulsion polymerization processes. The reactor vessel, equipped with ports for nitrogen flow, a condenser, stirrer, and monomer introduction was kept in a water bath maintained at 80°C. Prior to polymerization, the reaction mixture was purged with nitrogen, and during the reaction, a small positive pressure of nitrogen was maintained. The system was also subjected to constant downward stirring by a four-bladed stirrer rotating at 150 rpm.

The labeling of experiments was as follows: The first digit signaled the series, the second represented the particle growth stage, and the last number reflected the experimental number. For example, X3-137 represented the 137th reaction performed in this project and was the third step in a particle growth sequence.

### Seed Reaction

The synthesis of the seed followed the recipe given for X1-127 in Table I. The reactor vessel containing water only (350 g) was placed in a water bath at 80°C. The vessel was then purged with nitrogen for a period of not less than 30 min. Ammonium per-

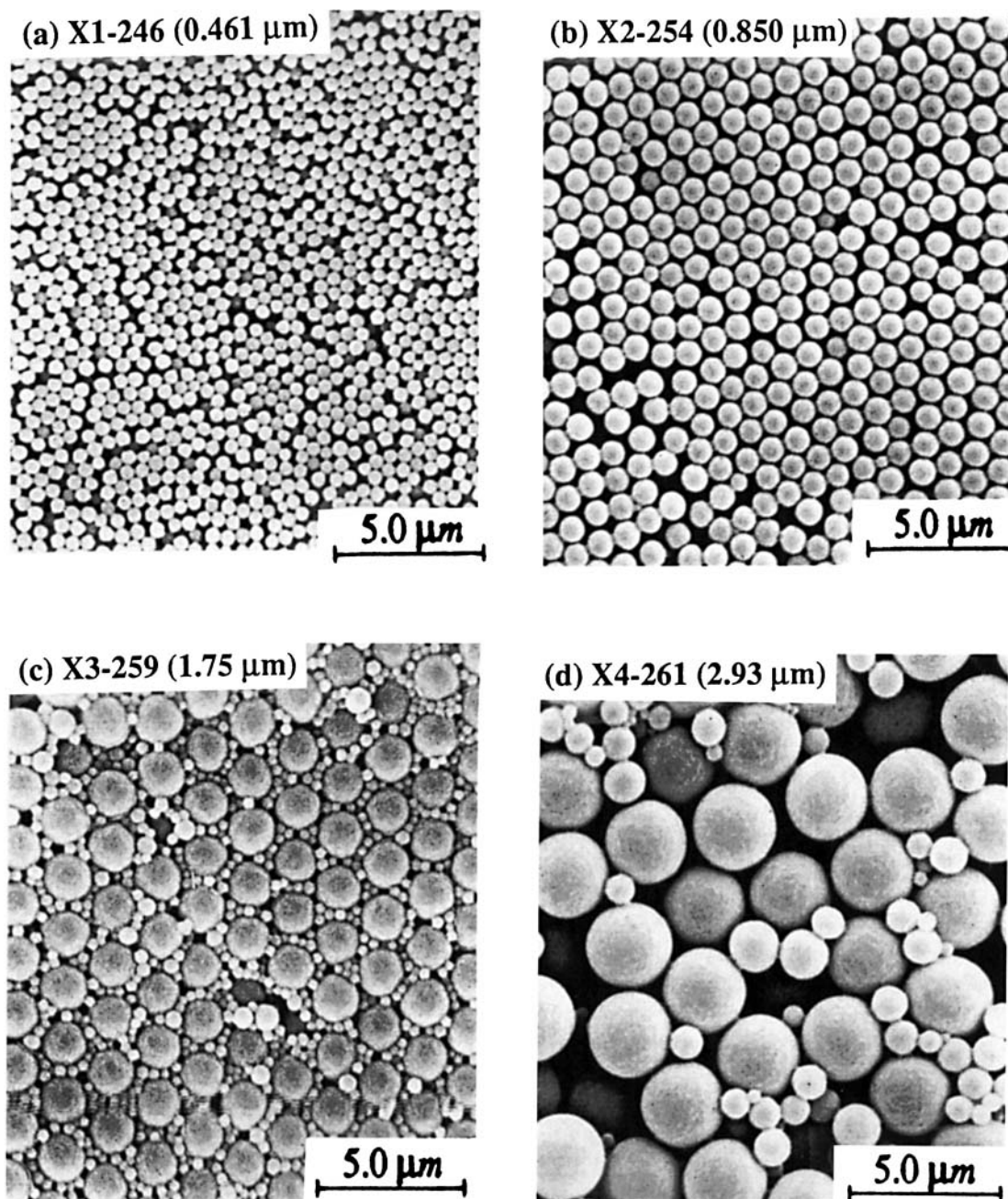
sulfate (1.00 g) was then added to the reactor vessel and the monomer feed consisting of MMA, BA, and IOMP was pumped into the reactor at a rate of 0.75 mL/min. After monomer addition was complete, the reaction was allowed to react for a further 2 h.

### Core Growth Stages

In step #4 (reaction X4-138 in Table I), seed (150 g), and water (310 g) were added to the reactor vessel and purged with nitrogen while being stirred at 150 rpm in a water bath at 80°C. The MMA (95.55 g), BA (54.45 g), IOMP (0.75 g), and AIBN (0.92 g) were weighed out and mixed. Prior to the start of the polymerization, a little AIBN (0.05 g) was added to the reactor to eliminate any incubation period. The monomer solution was then pumped in at a rate of 0.7 mL/min to the reactor. The AP (0.051 g) was weighed out and dissolved in water (40.0 g). This solution was then introduced to the reactor using a syringe pump so that addition was completed before the monomer feed finished. After the monomer addition was complete, 2 h were allowed for postreaction.

### Latex Characterization

Particles larger than 1.50  $\mu\text{m}$  were analyzed using 256 channels on a Coulter Multisizer II while those smaller were analyzed using a Joyce-Loebl Mark III disc centrifuge with water as the spin fluid. A Brookhaven Instruments Disc Centrifuge Particle Size Program calculated particle sizes and distributions from data obtained from the light scattering detector.



**Figure 1** SEM photographs of AP-initiated surfactant-free polymerizations.

Scanning electron microscopy (SEM) was performed on a Hitachi S-570 scanning electron microscope at an accelerating voltage of 15 keV. The samples were dried on a metal stub and then coated with gold prior to viewing. When looking for secondary particle populations, it was found that the edge of the drop was the best place to examine.<sup>1</sup>

Surface tension readings were obtained on a Cenco-DuNuoy Interfacial Tensiometer using the

ring method. The percent solids was determined gravimetrically.

## RESULTS AND DISCUSSION

In the emulsion polymerization, water-soluble initiators such as AP thermally decompose in the aqueous phase where the resulting radicals can add

**Table II** Reaction Series for Sequential Surfactant-free Seeded Emulsion Polymerizations Using AP Initiator

| Growth Step | Reaction | Dn ( $\mu\text{m}$ )<br>Primary Particles | Secondary Particles (SEM) | Surface Tension (dyne/cm) | Solids Concentration (wt %) |
|-------------|----------|-------------------------------------------|---------------------------|---------------------------|-----------------------------|
| 1           | X1-246   | 0.46                                      | No                        | —                         | 29.7                        |
| 2           | X2-254   | 0.85                                      | No                        | 55.4                      | 29.7                        |
| 3           | X3-259   | 1.75                                      | Yes                       | 54.5                      | 24.0                        |
| 4           | X4-261   | 2.93                                      | Yes                       | 53.9                      | 28.9                        |
| 5           | X5-262   | 4.10                                      | Yes                       | 47.8                      | 29.1                        |
| 6           | X6-263   | 5.17                                      | Yes                       | 46.5                      | —                           |

monomer units to form oligomeric species. These species will either collapse upon themselves or onto other insoluble material until a colloidal stable particle forms. This is described in the coagulative nucleation theory.<sup>2-4</sup> Stabilization of the particles is usually provided by surfactants which have been added to the system.

After nucleation and the formation of seed particles, particle growth continues as added monomer polymerizes on the existing particles. Seeded reactions can be used to grow particles to larger sizes by either swelling techniques<sup>5-8</sup> or by a series of semicontinuous polymerizations.<sup>9,10</sup> In copolymerizations such as ours, monomer reactivity ratios may cause compositional heterogeneity when swelling methods are used. If there is sufficient homopolymerization of the monomers involved, morphological heterogeneities such as core-shell arrangements,<sup>11-13</sup> dumbbell-shaped spheres,<sup>14</sup> or domains of one phase occluded in the other may result.<sup>12</sup> For these reasons, our MMA/BA particle growth was achieved by a series of semicontinuous seeded polymerizations. There are several factors which should be considered if one wishes to obtain monodisperse particles by this method: the polymer concentration, ionic strength, surface charge density, and particle number density.

Since the particle diameter increase is proportional to the cube root of the particle volume, a doubling of the particle diameter involves an eightfold increase in the polymer volume. At larger sizes, the diameter increase for a given amount of added polymer becomes quite small. Thus, to avoid lengthy growth stages, the particle number density (polymer particles per aqueous phase volume) is decreased with each successive growth stage to allow for more efficient increases in particle diameter. However, this leads to other problems.

The decrease in the particle number density increases the chances of secondary particle formation. Fewer particles exist and the ratio of polymer surface

area to aqueous phase volume slowly decreases over time. This makes the task of sweeping up any aqueous material before it is stabilized more difficult. To maintain a constant particle surface area to the aqueous phase volume ratio, the percent solids content would have to increase. At close to 30% solids content, these concentrations were already high for surfactant-free reactions, which are usually conducted at low percent solids.<sup>15</sup>

In electrostatically stabilized latexes, the ionic strength of the latex must be low enough so that the repulsive barrier between particles is not reduced to the point that particle coalescence occurs.

The surface charge density of the particles is also important. If there is not sufficient charge on the surface, the repulsive barrier will be too low. The surfactant level must then be above a certain minimum. If too much surfactant is present, the particle surface becomes completely covered and the excess surfactant will exist as free surfactant in the aqueous phase. This free surfactant may stabilize the polymer in the aqueous phase and prevent it from coalescing onto the seed particles. This leads to formation of secondary particles which then grow at the expense of the larger seed particles. Therefore, the surfactant levels must be carefully controlled.

In addition to surfactants, particle stability may also be enhanced by charged initiator residues on polymer chains. This makes it possible to develop polymerizations without a surfactant or so-called surfactant-free reactions.<sup>15-18</sup> In reactions initiated by AP, stabilization comes from either sulfate groups on polymer chains anchored on the particle surfaces or through sulfate groups on oligomeric material which may be surface-active. This latter material is termed an *in situ* surfactant (ISS).

There may be some sulfate groups from the AP that will not contribute to particle stability. These nonstabilizing entities include buried groups, undecomposed persulfate groups, aqueous phase oligomers without sufficient molecular weight to be sur-

Table III Reaction Series for Sequential Surfactant-free Seeded Emulsion Polymerizations

| Growth Stage # | Reaction | Initiator | Predicted Final Mol SO <sub>4</sub> <sup>-</sup> /m <sup>2</sup> (×10 <sup>-7</sup> ) | Surface Charge (μC/cm <sup>2</sup> ) | # SO <sub>4</sub> <sup>-</sup> Groups/nm <sup>2</sup> | Area per SO <sub>4</sub> <sup>-</sup> Group (nm <sup>2</sup> ) | Dn Primary Particles (μm) | Secondary Particles (SEM) | Final Surface Tension (dynes/cm) | Solids Concentration (Wt %) |
|----------------|----------|-----------|---------------------------------------------------------------------------------------|--------------------------------------|-------------------------------------------------------|----------------------------------------------------------------|---------------------------|---------------------------|----------------------------------|-----------------------------|
|                |          |           |                                                                                       |                                      |                                                       |                                                                |                           |                           |                                  |                             |
| 1              | X1-127   | AP        | 52.8                                                                                  | 50.9                                 | 3.18                                                  | 0.31                                                           | 0.475                     | No                        | 57.4                             | 30.0                        |
| 2              | X2-130   | AIBN      | 15.0                                                                                  | 14.5                                 | 0.90                                                  | 1.11                                                           | 0.817                     | No                        | 64.5                             | 29.0                        |
| 3              | X3-132   | AIBN      | 5.76                                                                                  | 5.55                                 | 0.35                                                  | 2.88                                                           |                           | Coagulated reaction       |                                  |                             |
| 3              | X3-137   | AP/AIBN   | 11.6                                                                                  | 11.2                                 | 0.70                                                  | 1.43                                                           | 1.39                      | No                        | 63.5                             | 29.8                        |
| 4              | X4-138   | AP/AIBN   | 10.0                                                                                  | 9.65                                 | 0.60                                                  | 1.66                                                           | 2.26                      | No                        | 64.1                             | —                           |
| 5              | X5-139   | AP/AIBN   | 9.97                                                                                  | 9.62                                 | 0.60                                                  | 1.67                                                           | 3.81                      | No                        | —                                | 27.1                        |
| 6              | X6-141   | AP/AIBN   | 10.2                                                                                  | 9.84                                 | 0.61                                                  | 1.63                                                           | 5.49                      | Yes                       | 64.5                             | 26.6                        |
| 7              | X7-142   | AP/AIBN   | 11.4                                                                                  | 11.0                                 | 0.69                                                  | 1.46                                                           | 6.74                      | Yes                       | —                                | 23.4                        |
| 8              | X8-143   | AP/AIBN   | 9.73                                                                                  | 9.39                                 | 0.58                                                  | 1.71                                                           | 8.44                      |                           | Coagulated reaction              |                             |

face-active, and the possible reaction [eq. (1)] of the sulfate radical with water to form a bisulfate ion and hydroxyl radical. The hydroxyl radical may still initiate polymerization, but this would lead to a chain end without electrostatic stabilization capability:

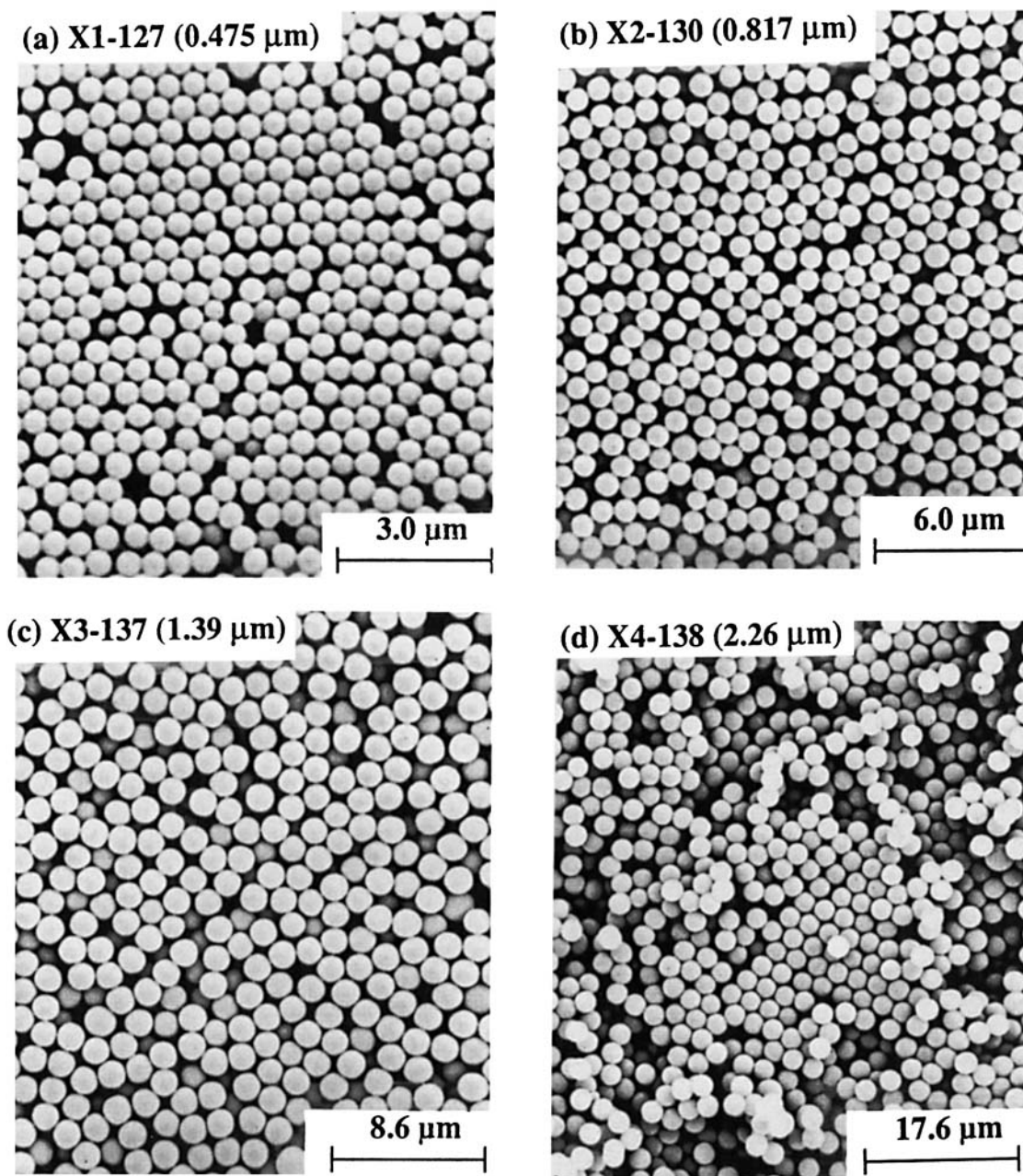


The existence of such nonstabilizing moieties may be ignored for practical purposes. The acid-catalyzed hydrolysis of sulfate groups to hydroxyl groups, which, in turn, may be oxidized to carboxyl groups has also been ignored. Although the hydroxyl groups are nonstabilizing, the carboxyl groups may provide some electrostatic stabilization provided that the pH is high enough. Carboxyl groups may also form from the hydrolysis of monomer ester linkages on the polymer.<sup>19</sup>

It has been assumed that all sulfate groups anchored on polymer chain ends can migrate to the particle surfaces. While this is not always the case,<sup>20,21</sup> a chain transfer agent, IOMP, had been added to our polymerizations in order to eliminate crosslinking which had been occurring due to chain transfer to BA units in the polymer.<sup>22</sup> At the reaction temperature of 80°C, there is sufficient chain mobility for many sulfate endgroups to remain on the surface, thus reducing the number of buried sulfate groups.

A series of sequential semicontinuous reactions using only the AP initiator at constant amounts was performed (Table I). As shown by the SEM photos in Figure 1, secondary particles appeared in the third growth step (X3-259). Therefore, the *in situ* surfactant (ISS) level must be controlled in a similar fashion to the level of added surfactants. The amount of ISS produced was more than enough to stabilize the particles. The low surface tension readings in Table II show that the amount of free surfactant in the latex was significant. In accordance with the smaller increases in particle surface area with each successive growth step, the amount of AP needed to be decreased. This decrease would, however, reduce the initiator/monomer ratio, thereby affecting the molecular weight and rate of polymerization.

These complications can be overcome by the use of nonionic oil-soluble initiators, such as AIBN, which shift the locus of polymerization away from the aqueous phase. Any oligomers produced in the water phase would be swept up by the main seed particles as they would not have any stabilizing ionic endgroups. In the absence of these stabilizing endgroups, all stabilization must come from surfactants whose concentration must be carefully monitored



**Figure 2** SEM photographs of AP/AIBN-initiated surfactant-free polymerizations.

so as not to stabilize secondary particles. Often, these surfactants are not desired since they introduce impurities to the latex. Thus, AIBN alone cannot initiate surfactant-free reactions. Therefore, one may compromise by using an AP/AIBN initiator combination whereby AP is added to provide the stabilization while the AIBN performs the bulk of the initiation (Table III).

The amounts of AP needed were calculated empirically for our semicontinuous MMA/BA copolymerization. Initially, the seed (X1-127) was synthesized using only the water-soluble AP initiator.

The number of sulfate groups could then be calculated assuming complete initiator decomposition. The number of polymer particles was determined by dividing the total polymer volume by the volume of one particle and the resulting figure then multiplied by the surface area of each particle to obtain the total polymer surface area. This led to the ratio of moles of sulfate groups to polymer surface area which was  $52.8 \times 10^{-7}$  mol sulfate group per meter squared for the seed latex (see Appendix 1). Using Faraday's constant, this could be converted to a surface charge density value in  $\mu\text{C}/\text{cm}^2$ .

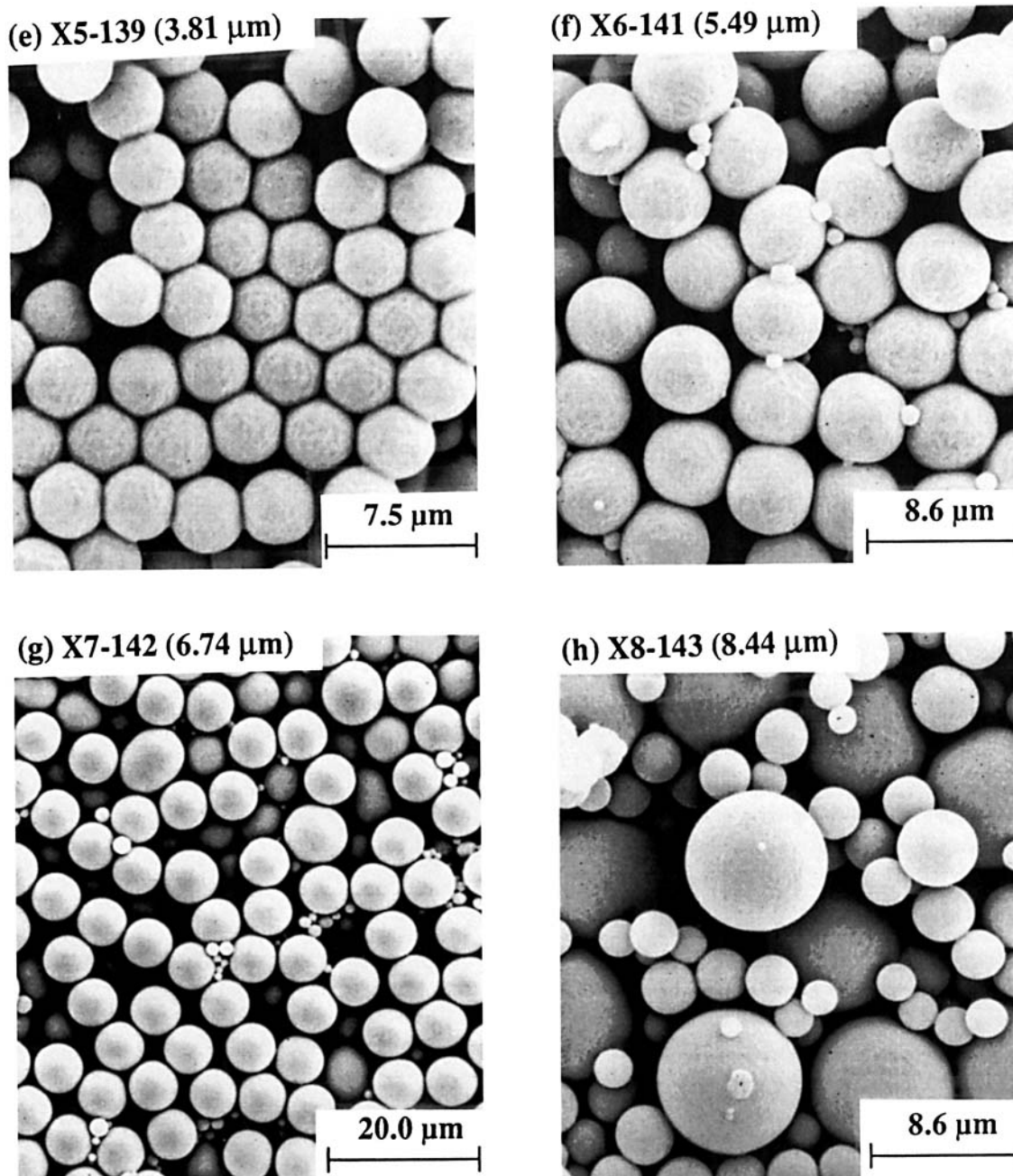


Figure 2 (Continued from the previous page)

Since the surface charge density of these particles was high ( $50.9 \mu\text{C}/\text{cm}^2$  at 100% initiator efficiency), only AIBN was used in the next growth step where the X1-127 seed particles were grown to produce X2-130 particles with no additional stabilization provided. All stabilization came from ISS or anchored groups on the seed latex. With a constant number of stabilizing groups and an increasing particle surface area, the surface charge density decreased to  $14.5 \mu\text{C}/\text{cm}^2$ . This value was still high enough for particle stabilization. The surface tension

increased, probably because free ISS in the aqueous phase was adsorbed onto the growing polymer particles.

The X2-130 latex was then used as the seed for a third growth stage, where, again, AIBN was the only initiator used. Toward the completion of the monomer feed, massive coagulation of the latex occurred, indicating that there was insufficient stabilization of the particles ( $5.55 \mu\text{C}/\text{cm}^2$ ). In these surfactant-free reactions, this implied that more AP was needed. Thus, taking account of the surface

charge density of the successful X2-130 and the unsuccessful X3-132, an intermediate value of  $11.2 \mu\text{C}/\text{cm}^2$  was arbitrarily picked as the minimum surface charge density needed for stabilization of the MMA/BA copolymers synthesized in these reactions. This number was then multiplied by the anticipated increase in the total surface area of polymer particles over the course of the reaction to get the moles of sulfate groups added. This could then be converted to the mass of AP needed, knowing that each mol of AP decomposes to form 2 mol of sulfate groups.

The surface charge density value quoted above assumes that all the resulting sulfate groups from a completely decomposed AP initiator contributed to the stability of the latex either through ISS or anchored groups. Since this is not the case, the numbers calculated in this article need to be multiplied by a constant representing the fraction of sulfate groups contributing to stabilization. No attempt was made to calculate what this constant might be for this system, since the process can be operated efficiently without this correction.

The AP was introduced to the polymerization slowly over the course of the reaction in accordance with the increase in particle surface area. From the SEM photos in Figure 2, it can be seen that monodisperse particles with diameters of  $3.8 \mu\text{m}$  were synthesized in five steps. The sixth step resulted in secondary particles as the particle number density was probably too low to sweep up the newly formed polymer. Despite this, particles with number-average diameters of  $8.4 \mu\text{m}$  were synthesized, although the latex was polydisperse. The amount of coagulum formed increased as well, since the amount of AP needed was underestimated by not allowing for the stabilization requirements of the secondary particles. This is reflected in the decreased solids content in growth step 8.

## CONCLUSIONS

It has been shown that the combination of a water-soluble and an oil-soluble initiator can lead to the surfactant-free production of monodisperse  $3.8 \mu\text{m}$  particles at 30% solids. In the successful reactions, the particle surface charge density was about  $10 \mu\text{C}/\text{cm}^2$  and the surface tension of the latex at about 63 dynes/cm. At larger sizes, even these criteria were not enough to maintain a stable monodisperse latex. Particles with diameters of  $8.4 \mu\text{m}$  were formed in eight sequential steps, although there were other smaller particles present.

The water-soluble/oil-soluble initiator combination could be extended to initiators other than AP and AIBN. A water-soluble initiator which imparts carboxylic stabilization may be desired for special surface applications. A mixture of azo initiators such as AIBN and the water-soluble, azobiscyanovaleric acid would result in only a single type of surface group.

Two of the authors (K. O'C. and A. R.) thank the Natural Science and Engineering Research Council of Canada and Xerox Research Centre of Canada for a Cooperative Research and Development grant. K. O'C. would also like to thank the Ontario Centre for Materials Research for a Cooperative Research Scholarship.

## APPENDIX

One can reduce the calculation for the anticipated final polymer surface area to the following relationship where subscripts  $f$  and  $s$  refer to final and seed, respectively:

$$\begin{aligned} (\text{Surface area})_f &= \frac{6(\text{polymer mass})_f^{2/3}(\text{polymer mass})_s^{1/3}}{(\text{polymer density})(\text{diameter})_s} \end{aligned}$$

The amount of  $\text{SO}_4^-$  groups required can then be calculated:

$$\begin{aligned} (\text{Mol SO}_4^-)_{\text{required}} &= (\text{mol SO}_4^-/\text{surface area})_{\text{required}} \times (\text{surface area})_f \end{aligned}$$

Subtraction of the amount already in the seed gives the amount to be added:

$$\begin{aligned} (\text{Mol SO}_4^-)_{\text{added}} &= (\text{mol SO}_4^-)_{\text{required}} - (\text{mol SO}_4^-)_{\text{seed}} \end{aligned}$$

## REFERENCES

1. Y. Chung-Li, J. W. Goodwin, and R. H. Ottewill, *Progr. Colloid Polym. Sci.*, **60**, 163 (1976).
2. R. M. Fitch and C. H. Tsai, in *Polymer Colloids*, R. M. Fitch, Ed., Plenum, New York, 1971.
3. P. J. Feeney, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **17**, 2520 (1984).
4. G. Lichti, R. G. Gilbert, and D. H. Napper, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 269 (1983).
5. J. Ugelstad, P. C. Mork, K. H. Kaggerud, T. Ellingsen, and A. Berge, *Adv. Coll. Int. Sci.*, **13**, 101 (1980).



6. J. Ugelstad, A. Berge, T. Ellingsen, R. Schmid, T.-N. Nilsen, P. C. Mork, P. Stenstad, E. Hornes, and O. Olsvik, *Prog. Polym. Sci.*, **17**, 87 (1992).
7. M. Okubo, M. Shiozaki, M. Tsujihiro, and Y. Tsukuda, *Colloid Polym. Sci.*, **269**, 222 (1991).
8. M. Okubo and M. Tsujihiro, U.S. Pat. 4,996,265 (1991).
9. J. W. Vanderhoff, M. S. El-Aasser, F. J. Micale, E. D. Sudol, C. M. Tseng, A. Silwanowicz, D. M. Kornfeld, and F. A. Vicente, *J. Dispers. Sci. Tech.*, **5**, 231 (1984).
10. D. G. Cook, A. Rudin, and A. Plumtree, *J. Appl. Polym. Sci.*, **46**, 1387 (1992).
11. D. I. Lee and T. Ishikawa, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 147 (1983).
12. I. Cho and K. W. Lee, *J. Appl. Polym. Sci.*, **30**, 1903 (1985).
13. S. Lee, PhD Thesis, University of Waterloo, 1991.
14. T. I. Min, A. Klein, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2845 (1983).
15. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Br. Polym. J.*, **5**, 347 (1973).
16. M. Chainey, M. C. Wilkinson, and J. Hearn, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 171 (1982).
17. T.-C. Pan, J.-F. Kuo, and C.-Y. Chen, *Polym. Eng. Sci.*, **31**, 916 (1991).
18. P. J. Feeney, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **20**, 2922 (1987).
19. R. M. Fitch, C. Cajria, and P. J. Tarcha, *J. Colloid Interface Sci.*, **71**, 107 (1979).
20. M. S. El-Aasser, F. V. Loncar, Jr., and J. W. Vanderhoff, *Makromol. Chem. Suppl.*, **10/11**, 335 (1985).
21. J. A. Masa, L. Lopez de Arbina, and J. M. Asua, *J. Appl. Polym. Sci.*, **48**, 205 (1993).
22. P. A. Lovell, and T. H. Shah, *Polym. Mater. Sci. Eng.*, **64**, 278 (1991).

Received October 27, 1994

Accepted May 23, 1995