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# Emulsion Polymerization of Styrene and Methyl Methacrylate Using Cationic Switchable Surfactants

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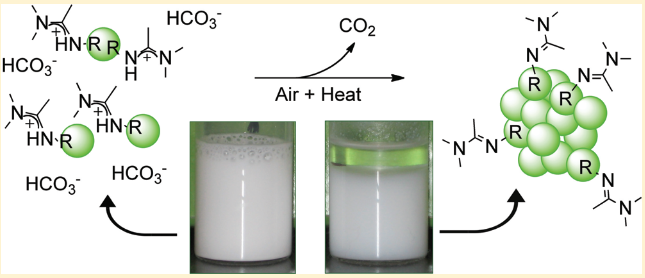
**ABSTRACT:** Colloidal latexes of polystyrene and poly(methyl methacrylate) have been prepared by emulsion polymerization using cationic amidine-based switchable surfactants. Particles with sizes ranging from 50 to 350 nm were obtained and the effect of factors such as initiator type, initiator amount, surfactant amount, and solid content on the particle size and ζ-potential of the resulting latexes have been examined. Destabilization of the latexes, which is commonly achieved by addition of salts or either strong acids for anionically stabilized latexes or alkalis for cationically stabilized latexes, requires only air and heat, which destabilize the latex by removing $CO_2$ from the system and switching the active amidinium bicarbonate surfactant to a surface inactive amidine compound. The resulting micrometer-sized particles can be easily filtered to yield a dry polymer powder and a clear aqueous phase.



## INTRODUCTION

Emulsion polymerization is extensively used to synthesize polymer colloids. It offers several advantages over conventional polymerization in that enhanced rates and high molecular weight are obtained and the reactions are carried out in water rather than volatile organic solvents.[1−3] If the desired product is a polymer latex, little further modification of the system is necessary, but if a dry polymer powder is desired, the latex must be destabilized. Latex destabilization is often carried out industrially using salts, acids for anionically stabilized latexes, or alkali for cationically charged latexes.[1−3] The ability to rapidly and easily alter the polymer dispersion from a suspended to an aggregated state without using salt or acid could provide significant environmental and economic benefits. Furthermore, the continued presence of surfactants in the polymer dispersion can in some cases negatively affect the final performance of the material. A preferred approach would be to use a surfactant capable of being switched off when its latex-stabilizing ability is no longer needed; such surfactants are termed "switchable surfactants". Herein we demonstrate polymer colloids whose latex stability depends on the continued presence of carbon dioxide. Among other applications, polymer colloids stabilized by these switchable surfactants could potentially be used as fast-drying paints, used for example on roads and highways. This would avoid the release of toxic fumes coming from ammonia, the release of which is currently used to accelerate film formation.[4,5]

Switchable surfactants have surface activity that can be reversibly altered in response to common triggers such as light,[6,7] pH,[8,9] or redox reagents.[10−18] Many switchable surfactants developed to date contain either ferrocenyl[10,11,13−16] or viologen[12] moieties, whose switchabilities are derived from their redox behavior. While these surfactants demonstrate the concept of switchability, they are not viable from an industrial or environmental standpoint due to the presence of expensive or toxic moieties and because the trigger for switching the surfactant is typically addition of further chemicals such as oxidants and reductants that could cause product contamination and result in unnecessary waste production. Furthermore, reported switchable surfactants based on photochemical azobenzenes[6,7] are not feasible in the case of emulsion polymerization due to the nontransparency of the resulting latex.

Carbon dioxide has been used as a trigger for latex destabilization when the dispersion is stabilized by anionic, fatty acid type surfactants.[19] It was shown in 1985 by Moore that polymerization of monomer emulsions stabilized by these surfactants yields polymer latexes that can be destabilized with the application of $CO_2$ followed by high shear. In this case, carbonic acid protonates the surfactant and decreases the electrostatic barrier between particles, causing aggregation. More recently, cationic switchable surfactants containing amidinium bicarbonate head groups have been synthesized[20] whose surfactancy can be switched off by removing carbon dioxide from the system. Removing $CO_2$ converts the surfactant to a neutral amidine, again decreasing the electrostatic barrier toward particle aggregation. The removal of $CO_2$ is best achieved by bubbling air, nitrogen, or argon through the polymer latex at slightly elevated

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temperatures. From an environmental standpoint, the use of air as a coagulant is preferable to the currently used high concentrations of salts, acids, or alkali.

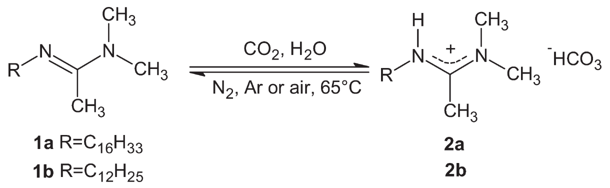
Colloidal polymer systems stabilized by switchable surfactants can be destabilized by switching the surfactant to a form that has little surface activity, leading to bulk separation of the two phases. This idea was recently mentioned in our preliminary communication,[20] where we used surfactant **2b** (Scheme 1) to stabilize micrometer-sized colloidal polystyrene particles. These latexes could be treated with Ar and heat followed by centrifugation and filtration to yield a dry polymer powder and a clear aqueous layer. No further addition of chemicals is necessary to bring about this latex destabilization, which simply occurs with the removal of $CO_2$.

This paper explores the emulsion polymerization of styrene and methyl methacrylate using amidine switchable surfactants. A key difference and improvement in this work versus the previous work is that latexes can now be prepared with particle sizes in the nanometer range versus the micrometer range, making this a true emulsion polymerization system. The process described in our previous paper was a microsuspension polymerization, with particle diameters ~20 $\mu$m. We have explored the factors (initiator type, initiator amount, surfactant amount, and solids content) that affect particle size and latex stability, as well as the role of the amidine surfactant in determining these properties. An understanding of the factors that affect controlled latex destabilization is required in order to induce phase separation in an effective manner, so that this process could become industrially viable.

## EXPERIMENTAL SECTION

**Reagents.** $CO_2$ (Praxair, Medical grade), $N_2$, and argon (Praxair, 99.998%) were used as received. 2,2′-Azobisisobutyronitrile (AIBN), 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061), and 2,2′-azobis-[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Styrene (99%) and methyl methacrylate (MMA) (99%) containing monomethyl ether hydroquinone (MEHQ) and 4-*tert*-butylcatechol (TBC) inhibitors, respectively, were purchased from Aldrich. Surfactants **2a** (*N*′-hexadecyl-*N,N*-dimethylacetamidinium bicarbonate) and **2b** (*N*′-dodecyl-*N,N*-dimethylacetamidinium bicarbonate) were synthesized as described previously.[20] Inhibitor removal columns (also purchased from Aldrich) were used to purify the monomers.

Scheme 1. Reaction of Long Chain Alkyl Amidines with $CO_2$ To Form Amidinium Bicarbonates



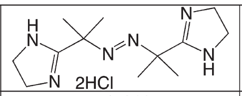
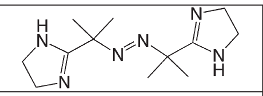
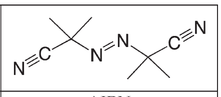
**Emulsion Polymerization.** Carbonated water was prepared by bubbling carbon dioxide for 30 min through a needle into a round-bottom flask containing distilled water. Emulsion polymerization reactions were carried out in 50 mL round-bottomed flasks equipped with a stir bar and a condenser or using a 12 reaction station carousel from Radley's Innovation Technology (model 201-2958). Typical reaction conditions are as follows: **2a** or **2b** was added to styrene or MMA in a 20 mL scintillation vial and sonicated using a Fisher Scientific ultrasonic cleaner (model FS30) for approximately 1 min to dissolve the surfactant. The surfactant solution was then added to the carbonated water in the round-bottomed flask while continuing to bubble $CO_2$ through the mixture using a needle. This was allowed to stir for 30 min at room temperature to form an emulsion. The initiator was dissolved in the monomer phase, distilled water, or carbonated water in the cases of AIBN, VA-044, or VA-061, respectively. The initiator solutions were added to the emulsion, after which polymerization was carried out at 65 °C for 5 h. When a round-bottomed flask was used, $CO_2$ was continuously bubbled through the emulsion throughout the polymerization. When the carousel reactor was used, the liquid was flushed with $CO_2$ and the vessel was then sealed.

An example of the conditions used to produce the latex in entry 11 of Table 3 is as follows: Methyl methacrylate (6.26 g, 62.5 mmol) was added to **2b** (Scheme 1, 14 mg, 0.044 mmol) and the mixture was sonicated to dissolve the surfactant. This mixture was added to 18 mL of carbonated water in a 50 mL round-bottomed flask and an emulsion was allowed to form over 30 min. In a separate vial, carbonated water (2 mL) was added to VA-061 (11 mg, 0.044 mmol) and the resulting clear solution was added dropwise to the emulsion. The emulsion was heated for 5 h at 65 °C with continuous bubbling of $CO_2$. These reaction conditions produced a latex with a particle size of 159 nm and a ζ-potential of 33 mV. Conversion of monomer to polymer was determined gravimetrically to be 97%. The molecular weight and polydispersity of the polymer was determined using gel permeation chromatography (GPC). The system was a Viscotek GPCmax VE 2001 containing a PAS-106 M mixed bed column (from the PolyAnalytik SupeRes Series), coupled with a Viscotek 3580 differential refractive index detector (calibrated with PS standards ranging from 6.90 to 860 kg $mol^{-1}$). THF was used as the eluent with a flow rate of 1.0 mL $min^{-1}$. The number average molar mass ($M_n$), weight average molar mass ($M_w$), and the molecular weight distribution (MWD) of the PMMA synthesized above were determined to be 180 kg $mol^{-1}$, 956 kg $mol^{-1}$, and 5.30, respectively.

**Latex Destabilization.** Colloidal latexes of polystyrene (PS) and poly(methyl methacrylate) (PMMA) prepared as described above were destabilized by continuous bubbling of a nonacidic gas (Ar, air, or $N_2$) through the latex at 65 °C using a needle while the sample was stirred. The polymer particles were either left to settle under gravity or centrifuged for 10 min at 3500 rpm.

**Latex Characterization.** To determine overall conversion and conversion over time, 1−2 g samples of latex were removed from the reaction vessel via syringe and were allowed to dry under a flow of air for 24 h followed by oven drying for 24 h at 85 °C.

Table 1. Stability of Polystyrene Latexes Formed Using 2a and Different Azo-Based Initiators[a]

| |  |  |  |
|---|---|---|---|
| Initiator Name | VA-044 | VA-061 | AIBN |
| Particle Size (nm) | 82 | 65 | >6000 |
| Conversion (%) | 93 | 81 | - |
| Latex Stability[b] | Stable | Stable only in the presence of $CO_2$ | Unstable |

[a] Reactions were carried out for 5 h at 65 °C. [b] Stability was determined visually. Samples where no visible settling occurred for at least 2 weeks were deemed stable.

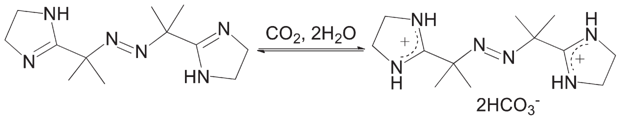
Conversion was determined using the following equation

$$\%\text{conversion} = \frac{m_{\text{dried polymer}} m_{\text{TOT}}}{m_{\text{latex sample}}[m_{\text{monomer}} + m_{\text{surfactant}} + m_{\text{initiator}}]} \times 100$$

where $m_{\text{dried polymer}}$ is the mass of the dried polymer; $m_{\text{TOT}}$ is the total mass of water, monomer, surfactant, and initiator; $m_{\text{latex sample}}$ is the mass of the latex sample removed; and $m_{\text{monomer}}$, $m_{\text{surfactant}}$, and $m_{\text{initiator}}$ are the initial masses of the monomer, surfactant, and initiator, respectively.

Particle size was determined using a Malvern Mastersizer 2000 (size range from 0.05 to 2000 $\mu$m) equipped with a Hydro2000S optical unit and/or a Zetasizer Nano ZS (size range from 0.6 nm to 8.9 $\mu$m). The instrument that was used depended on the particle size of the sample. The particle sizes of the latex samples were typically at the lower end of the size range for the Mastersizer 2000, so the Zetasizer Nano ZS was used. After destabilization, the particle size fell at or above the upper end of the Zetasizer Nano ZS size range, necessitating the use of the Mastersizer 2000. ζ-Potentials were determined using a Zetasizer Nano ZS. Latex samples were diluted with distilled water presaturated with carbon dioxide, and measurements were taken using a disposable capillary cuvette. SEM images were acquired using a Hitachi S-5200 scanning electron microscope.

**Scheme 2. Reaction of VA-061 with Carbon Dioxide and Water To Produce the Bicarbonate Salt**



VA-061 3

## RESULTS AND DISCUSSION

**Emulsion Polymerization.** Emulsion polymerization of styrene was carried out using **2a** as a surfactant with a variety of azo-based free radical initiators to determine the stability and particle size of the resulting polymer latexes and to determine which initiator would be most compatible with facile aggregation of the latex particles upon removal of CO$_2$. The ideal latex should have submicrometer polymer particles, be stable in the presence of CO$_2$, and be unstable when CO$_2$ is removed. Table 1 shows the results obtained with surfactant **2a** and each of the three initiators that were investigated. When choosing an initiator, the most important criteria is that it not be anionic, so there will be no attractive interactions between the initiator end groups on the particle surface with the cationic surfactant.

Latex generated using the cationic, water-soluble initiator VA-044 showed no visible signs of polymer settling after the removal of CO$_2$. Even after treatment of the latex with heat and air, followed by centrifugation for 10 min at 3500 rpm, the polymer

**Table 2. Variation in Particle Size and ζ-Potential of Polystyrene Latexes Using Different Solid Contents, Surfactant Concentrations, and Initiator Concentrations**[a]

| entry no. | wt % styrene[b] | mol % **2b**[c] | mol % **3**[c] | particle size, nm (PdI)[d] | ζ-potential, mV | % conversion | % coagulum |
|---|---|---|---|---|---|---|---|
| 1 | 13.5 | 1.00 | 1.00 | 72 ± 0.1<br>(0.05) | 51 ± 2 | 93 | 2 |
| 2 | 13.5 | 0.50 | 0.50 | 129 ± 1<br>(0.01) | 45 ± 1 | 89 | 0 |
| 3 | 13.5 | 0.25 | 0.25 | 198 ± 2<br>(0.02) | 49 ± 1 | 92 | 6 |
| 4 | 13.5 | 0.10 | 0.10 | 222 ± 2<br>(0.03) | 44 ± 0.3 | 85 | 2 |
| 5 | 13.5 | 0.25 | 0.50 | 203 ± 3<br>(0.04) | 59 ± 2 | 94 | 24 |
| 6 | 22.8 | 3.00 | 1.00 | 58 ± 1<br>(0.05) | 31 ± 2[e] | – | – |
| 7 | 23.5 | 1.00 | 1.00 | 61 ± 1<br>(1.2) | 59 ± 6 | 100 | 2 |
| 8 | 23.5 | 0.50 | 0.50 | 85 ± 1<br>(0.06) | 59 ± 1 | 95 | 3 |
| 9 | 23.5 | 0.25 | 0.25 | 203 ± 2<br>(0.03) | 54 ± 1 | 98 | 5 |
| 10 | 23.5 | 0.10 | 0.10 | 178 ± 2<br>(0.02) | 51 ± 1 | 94 | 7 |
| 11 | 23.5 | 0.50 | 0.25 | 94 ± 1<br>(0.08) | 55 ± 1 | 99 | 10 |
| 12 | 38.5 | 0.25 | 0.25 | 239 ± 2<br>(0.09) | 56 ± 2 | 87 | 53 |
| 13 | 38.5 | 0.10 | 0.10 | 372 ± 16<br>(0.19) | 45 ± 1 | 83 | 35 |

[a] Reactions were carried out for 5 h at 65 °C under 1 atm of CO$_2$. [b] With respect to water. [c] With respect to styrene. [d] Values of PdI obtained from the Zetasizer ZS that are <0.1 indicate a narrow, monomodal size distribution. [e] Measured using a dip cell (all others measured using a capillary cuvette).

**Table 3. Variation in Particle Size and ζ-Potential of PMMA Latexes Using Different Solid Contents, Surfactant Concentrations, and Initiator Concentrations**[a]

| | wt % MMA[b] | mol % **2b**[c] | mol % **3**[c] | Zetasizer particle size, nm (PdI) | Mastersizer[d] particle size, nm (uniformity)[e] | ζ-potential, mV | % conversion |
|---|---|---|---|---|---|---|---|
| 1 | 13.5 | 0.12 | 0.07 | 143 ± 1<br>(0.05) | – | 27 ± 2 | 99 |
| 2 | 13.5 | 0.07 | 0.07 | 183 ± 2<br>(0.04) | – | 35 ± 2 | 99 |
| 3 | 13.5 | 0.03 | 0.05 | 218 ± 1<br>(0.15) | 167<br>(0.511) | – | 96 |
| 4 | 23.5 | 2.00 | 1.00 | 47 ± 0.2<br>(0.06) | _ | 22 ± 1 | 97 |
| 5 | 23.5 | 2.00 | 0.50 | 41 ± 1<br>(0.06) | _ | 46 ± 1 | 86 |
| 6 | 23.5 | 0.50 | 1.00 | 58 ± 1[f]<br>(0.11) | _ | 53 ± 1 | 99 |
| 7 | 23.5 | 0.50 | 0.50 | 56 ± 1<br>(0.09) | _ | 48 ± 3 | 87 |
| 8 | 23.5 | 0.50 | 0.07[g] | 59 ± 0.3<br>(0.12) | _ | _ | _ |
| 9 | 23.5 | 0.25 | 0.07 | 101 ± 1<br>(0.09) | _ | 44 ± 2 | 86 |
| 10 | 23.5 | 0.12 | 0.07 | 134 ± 1<br>(0.07) | _ | 31 ± 2 | 92 |
| 11 | 23.5 | 0.07 | 0.07 | 159 ± 2<br>(0.1) | _ | 33 ± 0.5 | 97 |
| 12 | 23.5 | 0.03 | 0.05 | 244 ± 2<br>(0.27) | 316<br>(0.307) | _ | 88 |
| 13 | 38.5 | 0.03 | 0.05 | 227 ± 5<br>(0.38) | 319<br>(0.192) | _ | 93 |

[a] Reactions were carried out for 5 h at 65 °C under 1 atm of $CO_2$. [b] With respect to water. [c] With respect to monomer. [d] Particle size values obtained on the Zetasizer ZS are reliable as long the PdI values are less than 0.1. The Mastersizer was used to measure particle sizes of those samples having a particle size PdI > 0.15. [e] Higher values of uniformity indicate less uniform particle sizes. [f] Large amounts of coagulum were produced (as much as 50%). [g] VA-044 initiator was used.

particles remained suspended. The p$K_{aH}$ of the amidine shown in Scheme 1, where R = $C_6H_{13}$, has been reported to be 12.37[21] and is not expected to change appreciably with alkyl chain length. The p$K_{aH}$ of 2-ethylimidazoline, which is a fair representation of the end groups that result from initiator decomposition, is 11.05.[22] Since the surfactant is more basic, transfer of protons is expected to occur from the hydrochloride initiator to the surfactant resulting in sustained surface activity of **2a** (as **1a**·HCl) even in the absence of carbon dioxide.

AIBN was then chosen due to its neutral charge, thus eliminating the possibility for transfer of anions to the surfactant. It was found that latexes formed using this initiator had large particles and very broad size distributions, and thus it was deemed unsuitable for further investigation. This is most likely due to the oil solubility of AIBN, which promotes polymerization within the micrometer-sized monomer droplets, creating very large particles. Furthermore, oil-soluble initiators yield less stable latexes due to the lack of additional stabilizing charge from initiator end groups on the particle surface.

VA-061 is the neutral form of VA-044 (Table 1) and contains a cyclic amidine group that can react with $CO_2$ in the same way as **1a** and **1b**, producing the bicarbonate salt of 2,2′-azobis[2-(2-imidazolin-2-yl)propane], **3** (Scheme 2).[23] The water-soluble salt **3** can then be used as the initiator for the polymerization reaction, and upon treatment of the resulting latex with air and heat, we postulate that polymer particles containing these initiator end groups on the particle surface should be neutralized and the latex would be more easily aggregated. The initiator **3** was generated in situ prior to polymerization and has been used for all further investigations.

A series of PS latexes was prepared using the conditions shown in Table 2. The effects of solids content, initiator concentration, and surfactant concentration on particle size and ζ-potential were examined. It was found that the particle size was essentially independent of initiator concentration (entries 3 vs 5 and 8 vs 11). This is unexpected behavior, since higher initiator concentrations should favor nucleation of more micelles, thus producing a larger number of particles and therefore smaller particles compared to those produced at lower initiator concentrations.[2,3] The fact that the particle size is independent of initiator concentration suggests that the primary mode of particle generation in our system may be homogeneous, rather than micellar, nucleation.

In contrast, particle size was highly dependent on surfactant concentration; increases in particle size were observed when the surfactant concentration was decreased (entries 2 vs 5, and 9 vs 11).

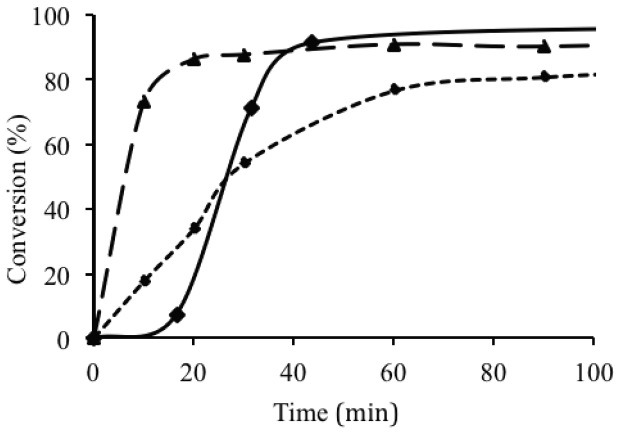


**Figure 1.** Conversion versus time profile for the polymerization of MMA using 1.0 mol % of **2b** and 1.0 mol % of **3** (— —); MMA using 0.07 mol % of **2b** and 0.07 mol % of **3** (—); and styrene using 1.0 mol % of **2b** and 1.0 mol % of **3** (- - -).

Simultaneously decreasing both the surfactant concentration and the initiator concentration also produced an increase in particle size (entries 1−4 and 7−10). This is expected behavior, as increasing the surfactant concentration increases the number of particles that can be stabilized, leading to smaller particle diameters. This effect has been noted numerous times in the batch emulsion polymerization of styrene using cationic surfactants.[24−27]

The particle size generally decreased with increasing weight percent of styrene (at constant ratios of surfactant to monomer and initiator to monomer) when the resultant latex contained <10% coagulum (entries 1−4 versus 7−10). This can be attributed to higher overall surfactant concentrations at higher styrene loadings.

Coagulum formation during polymerization was generally not a serious problem; most of the experiments produced <5% coagulum. However, it did become a problem at higher initial monomer concentrations. At 38.5 wt % of styrene, 53% of the resulting polymer was a large, white solid mass, rendering any conclusions about trends in particle size at higher initial styrene concentrations unreliable. ζ-Potential measurements in all cases indicate that the latexes should be stable, as they have values greater than 25 mV.

Polymerization of methyl methacrylate was also performed (Table 3). Although MMA is more hydrophilic and has a higher water solubility than styrene (159 versus 3.5 mmol $dm^{-3}$),[2] similar behavior between the monomers was observed. Decreasing the surfactant concentration increased the particle size (entries 1−2 and 8−11), and changes in the initiator concentration seemed to have little effect on particle size (entries 4 vs 5, and 6 vs 7). With all other ratios constant, increasing the solids content tended to slightly decrease the particle size (entries 1 vs 10, and 2 vs 11).

Conversion in all cases (for both styrene and MMA) was over 80%; typical conversion profiles can be seen in Figure 1. The curves show the standard shape associated with conventional batch emulsion polymerization. In the case of MMA polymerization, the induction time was longer when a lower initiator concentration (0.07 mol % versus 1.0 mol %) was used, leading to a longer time to reach maximum conversion, which was >95% in both cases.

Comparing the polymerization of styrene to that of methyl methacrylate, the particle size was larger in the case of polystyrene with otherwise equivalent conditions (Table 2, entry 8 versus Table 3, entry 7). The fact that PMMA is more hydrophilic than PS allows more surface to be stabilized by the same amount of surfactant, leading to a larger number of particles. The polymerization of styrene generally proceeded more slowly than that of MMA, produced more coagulum, and reached lower overall conversions.

**Table 4. Assessment of the Long Term Stability of PMMA Latexes Stabilized by 2b That were Exposed to Air and Those That Were Saturated with $CO_2$ for 30 min Once a Day for 7 Days**[a]

| | bubbling $CO_2$ for 30 min each day[b] | | no bubbling | |
|---|---|---|---|---|
| time, d | ζ-potential, mV | size, nm (PdI) | ζ-potential, mV | size, nm (PdI) |
| 3 | – | – | 52 ± 0.5 | – |
| 4 | 54 ± 0.4 | 59 (0.09) | 53 ± 1 | 58 (0.11) |
| 5 | 49 ± 1 | 59 (0.11) | 46 ± 3 | 58 (0.11) |
| 6 | 48 ± 2 | 59 (0.10) | 41 ± 4 | 59 (0.10) |
| 7 | 52 ± 2 | 59 (0.11) | 43 ± 2 | 59 (0.11) |
| 17 | – | 93 (0.21) | – | 10.4 $\mu$m |

[a] Measurements taken at room temperature. [b] $CO_2$ was bubbled through the latex each day until day 7, after which it was sealed under $CO_2$ for 10 further days.

**Long-Term Latex Stability.** Long-term stability of the latex formulated using the conditions in Table 3, entry 4 (2.0 mol % of **2b** and 1.0 mol % of **3**) was also assessed. The latex was divided into two samples, whose particle size and ζ-potential were measured each day for 1 week. The first sample was left under an atmosphere of $CO_2$ between measurements, and to ensure that the latex was saturated during the measurement, $CO_2$ was bubbled through it for 30 min prior to analysis. The second sample was stored in a vial that was opened to air each day and not treated with $CO_2$ prior to analysis. It was found that the latex which was saturated with $CO_2$ was stable (no changes in particle size or ζ-potential; see Table 4) for at least 1 week. After that, the sample remained capped and untouched for 10 more days and the particle size only increased slightly (from 59 to 93 nm). The sample of latex that was exposed to air and received no $CO_2$ treatment showed a slight decrease in ζ-potential throughout the first week. After 17 days, that sample became very viscous and turned to a gel (Figure 2). At this point, particle size was measured and it was determined that the latex was severely destabilized (the final particle size was 10.4 $\mu$m). From these results, we conclude that polymer latexes synthesized using amidine surfactants are stable as long as they are kept under an atmosphere of $CO_2$. Another important aspect worth noting is that the latexes are sufficiently stable that rigorous air-free conditions during synthesis are not necessary and that the latexes can be stored in air if stability is required for less than approximately 1 week.

**Latex Destabilization.** Many factors can affect the colloidal stability of a latex and it is necessary to understand these factors in order to determine how and when destabilization occurs. Particle aggregation occurs when the free energy barrier between polymer particles is overcome, rendering the interactions between particles more favorable than their interaction with the aqueous phase. Salts can be added to electrostatically stabilized latexes to suppress the electric double layer and decrease the energy barrier toward aggregation. Furthermore, if the surfactant is pH sensitive, addition of acids or bases will decrease surface charge, providing less stabilization and more rapid aggregation.[1,28]

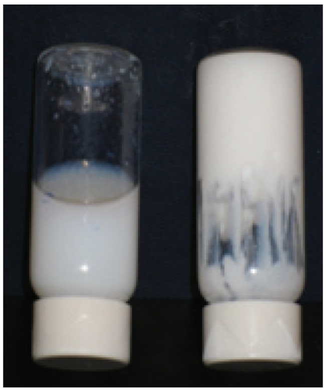


**Figure 2.** Photograph of PMMA latexes (prepared using 23.5 wt % of MMA, 2.0 mol % of **2b**, and 1.0 mol % of **3**) after 17 days with (at left) bubbling of $CO_2$ for 30 min each day for the first 7 days and (at right) no $CO_2$ bubbling (vials were inverted for the photograph to show the increased viscosity of the sample that received no $CO_2$ treatment).

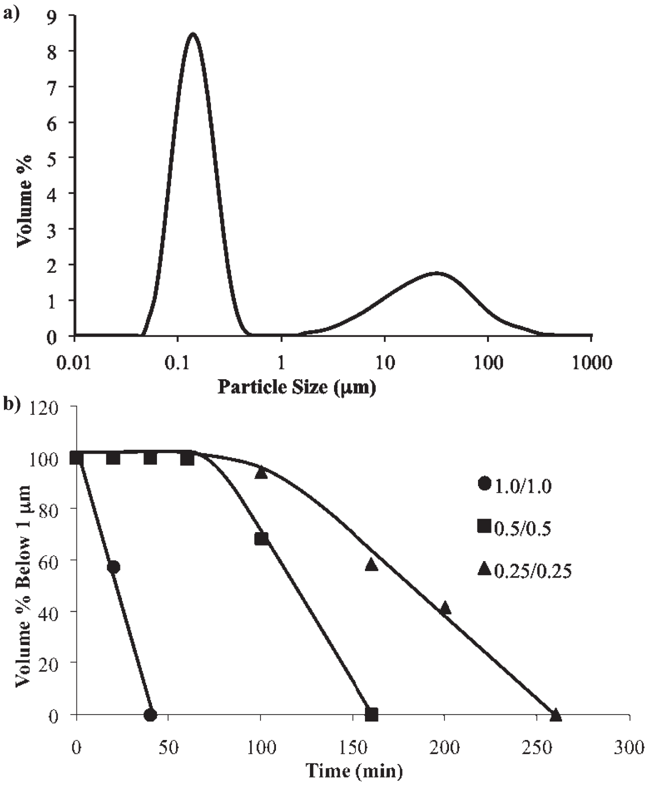


**Figure 3.** (a) Particle size distribution of a polystyrene latex synthesized using 0.5 mol % **2b** and 0.5 mol % **3** after treating with air at 65 °C for 100 min. (b) Volume percent of polystyrene aggregates over time in latexes containing various amounts of **2b** and **3** (mol % **2b**/mol % **3**) after treating with air at 65 °C (23.5 wt % polystyrene).

In the system currently under study, the surfactant is pH sensitive and has been designed to respond to the amount of $CO_2$ present. Removal of $CO_2$ causes neutralization of the surfactant, resulting in a decreased surface charge and a decreased electrostatic barrier. The chemical reaction converting the bicarbonate salt form of the surfactant to the neutral amidine is endothermic, and thus, the temperature of the system needs to be raised in order to cause aggregation. This temperature increase also increases the average particle kinetic energy and the rate of particle encounters, leading to an increased rate of particle aggregation.

The polystyrene latexes synthesized as reported in Table 2, entries 7−9 were destabilized by bubbling air through the samples at 65 °C. Figure 3 shows the results of this study and provides insight into the factors that affect destabilization. Figure 3a shows that a second peak appears at approximately 20 $\mu$m after bubbling with air and heating for 100 min, signifying the formation of stable polystyrene aggregates. In numerous experiments, we consistently observed this trend with the appearance of large aggregates but without observing intermediate particle sizes. Furthermore, the time that it takes for the sample to become destabilized depends on the amount of amidine functionality present in the system and the initial particle size, which can be seen in Figure 3b. At higher initial concentrations of **2b** and **3** (1.0 mol % each vs 0.25 mol % each), the volume percentage of particles below 1.0 $\mu$m (primary particles) decreases quickly with time. This implies that higher amidine concentrations favor destabilization. However, higher initial concentrations of **2b** and **3** also produce smaller initial particle sizes, so it is unclear whether small initial particle sizes or high surfactant/initiator concentrations lead to faster destabilization. If the bubbling and heating time is extended, no detectable primary particles remain, as is evident from the single monomodal peak in the micrometer range for each latex sample at 24 h.

Although a larger volume of stable aggregates is formed faster when amidine concentrations are high, the final particle size of the aggregates (in polystyrene latexes) after destabilization does not depend on the amount of amidine functionality on the particles. It appears to have a slight dependence on latex polymer concentrations, as the samples with higher solids content tend to produce larger final destabilized particle sizes.

PMMA latexes were destabilized using heat and either argon or air, and changes in particle size and $\zeta$-potential were monitored over time in the cases of Table 3 entries 4 and 11. When primary PMMA particles were small (47 nm, Table 3, entry 4), latex destabilization occurred rapidly and resulted in the formation of a polymer gel that was difficult to stir. Gel formation of latexes with small particles typically occurred at ~90 min. When water was added to the polymer gel, a mixture of latex and aggregated polymer particles resulted, and with further treatment of gas and heat, a clear water layer resulted after settling of polymer particles.

At larger primary particle sizes (159 nm, Table 3, entry 11), gel formation during destabilization does not occur although destabilization took much longer. This may be due to the fact that at larger primary particle sizes and the same polymer concentration there are fewer particles and therefore fewer particle−particle interactions, leading to a decreased rate of aggregation.

In our system, destabilization of the latex involves the removal of $CO_2$, which decreases the electrolyte concentration in the continuous phase, effectively increasing the thickness of the electric double layer surrounding the polymer particles. This has the effect of increasing the sample viscosity and allowing gel formation in the case of the latex sample with 47 nm particles. Smaller particles have a larger effective volume fraction and this is a possible explanation for gel formation in the small particle size latexes. The thickness of the double layer will be the same in the case of both the small and large particles, but the volume of the excluded layer surrounding the particle due to double layer repulsion will be a greater fraction of the total particle volume in the case of particles with smaller diameters. This can be

**Table 5. Variation in $\zeta$-Potential with Time during Switching off Procedure for Latex Formulated in Table 3, Entry 11 (23.5 wt % of MMA, 0.07 mol % of 2b, 0.07 mol % of 3)[a]**

| treatment time (min) | $\zeta$-potential (mV) |
|---|---|
| 0 | 42 ± 2 |
| 40 | 34 ± 1 |
| 80 | 27 ± 1 |
| 120 | 26 ± 0.4 |
| 160 | 24 ± 1 |

[a] Measurements taken at room temperature.

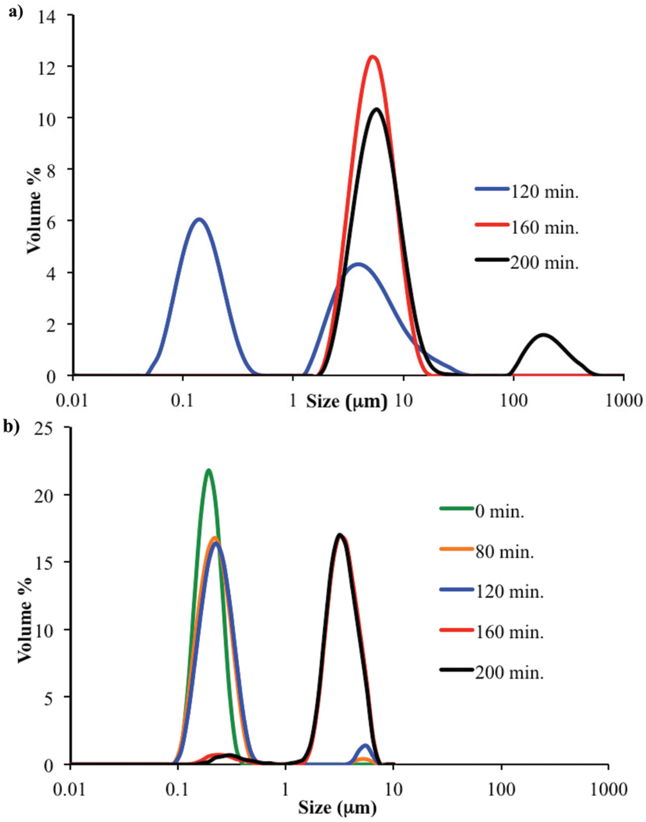


**Figure 4.** Change in particle size with time during destabilization of latex produced using conditions in Table 3, entry 11 (23.5 wt % of MMA, 0.07 mol % of **2b**, 0.07 mol % of **3**) monitored with the (a) Mastersizer 2000 and (b) Zetasizer ZS.

expressed mathematically using the following equation[29]

$$\phi_{\text{eff}} = [\phi(1 + 6d)/D]$$

where $\phi_{\text{eff}}$ is the effective volume fraction, $\phi$ is the polymer volume fraction, $d$ is the double layer thickness, and $D$ is the particle diameter. The change in double layer thickness upon $CO_2$ removal combined with the large effective volume fraction induces gel formation in the case of the 47 nm particles. Furthermore, the interparticle spacing is less with smaller particles, which excerbates the tendency to higher viscosity.

In the cases where gel formation did not occur, changes in particle size and $\zeta$-potential with time could be easily monitored. As expected, the $\zeta$-potential decreases with destabilization time (Table 5), indicating a decreased particle charge due to the surfactant and/or initiator end groups switching to their neutral form. The decrease in $\zeta$-potential corresponds to the growth of a new peak in the micrometer range as the particles begin to aggregate due to the decrease in electrostatic stabilization (Figures 4 and 5). This may not correspond to removal of all of the surface charge, but enough charge has been neutralized that van der Waals attractive forces between particles become larger than electrostatic repulsion forces. After air and heat treatment for 80 min, a second peak appeared in the micrometer range. Subsequent measurements were recorded using both the Zetasizer ZS and the Mastersizer 2000. The Zetasizer ZS is a dynamic light scattering instrument and is most useful and accurate for monomodal samples whose particle size is <1 $\mu$m. Because destabilization produces particles >5 $\mu$m, measurements were also taken on the Mastersizer 2000, a static light scattering instrument that can measure samples up to 2000 $\mu$m. An overlay plot of the particle size distributions after destabilization for various time intervals using both instruments can be seen in Figure 4. Final average particle sizes in the case of PMMA did not appear to depend on polymer concentration or amidine concentration and were all generally in the range of 6−7 $\mu$m. Extended treatment of polystyrene and PMMA latexes with air and heat caused further aggregation and sometimes produced particles with very large diameters (>100 $\mu$m).

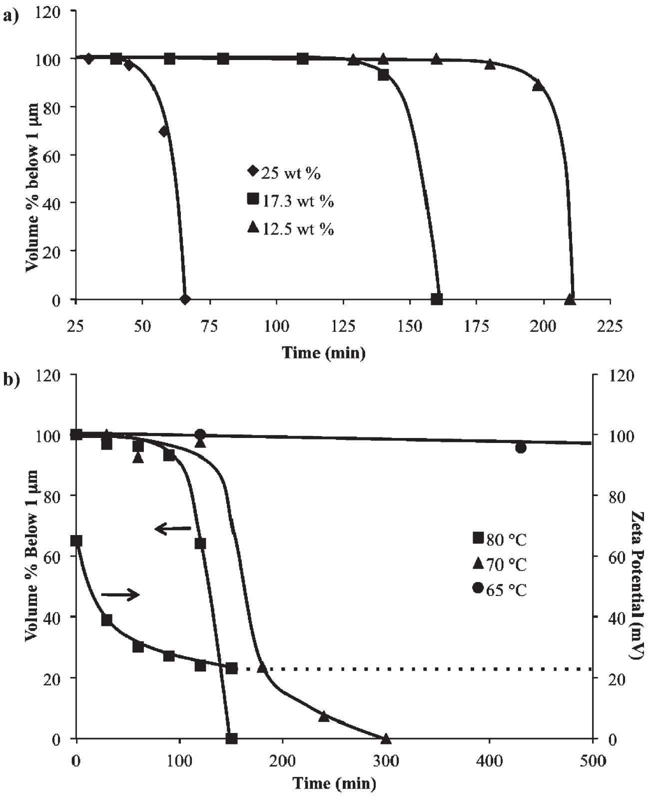


**Figure 5.** Volume percent of PMMA particles stabilized by **2b** below 1.0 $\mu$m over time after heating and bubbling with air at different (a) polymer concentrations (temperature is constant at 65 °C) and (b) temperatures (polymer concentration is constant at 5 wt %). The decrease in $\zeta$-potential over time corresponding to destabilization of PMMA particles at 80 °C is also shown.

The effect of polymer concentration and temperature on destabilization time was also examined, and the results of this study can be seen in Figure 5. At higher temperatures (80 °C) destabilization occurs much faster. Increasing latex temperature

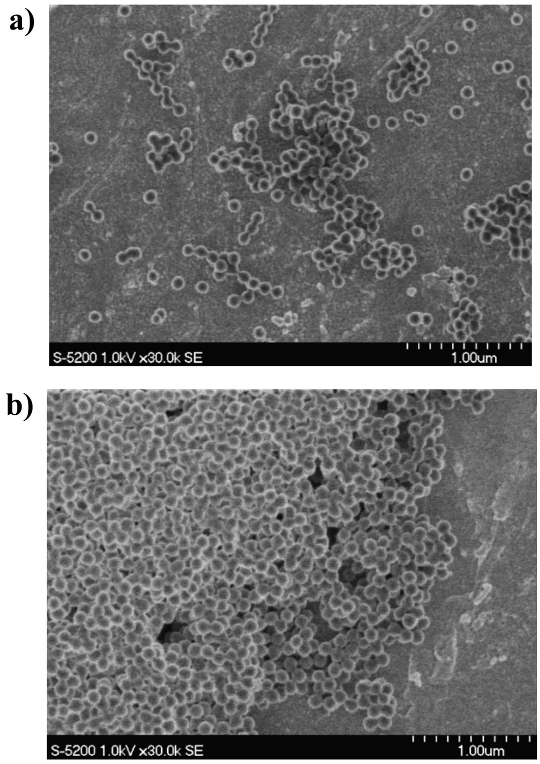


**Figure 6.** SEM images of particles from (a) a PMMA latex stabilized with **2b** and (b) a similar PMMA latex treated with air and heat to remove the $CO_2$. In both cases, the latex was prepared using 5 wt % of MMA, 0.12 mol % of **2b**, and 0.07 mol % of **3**.

increases the average kinetic energy of particles and the frequency of collision between them. Thermal energy of the particles increases with temperature, and this allows two particles to surmount the potential energy barrier that may exist between them and allows them to aggregate together. At higher polymer concentrations (25 wt %), aggregation also occurs much faster. This again is due to the decrease in particle spacing, thus increasing the frequency of particle collisions and promoting aggregation.

SEM images were obtained of a PMMA latex before and after the destabilization procedure. The latex before the destabilization procedure shows primary particles with some aggregation (Figure 6a), which is most likely due to the evaporation of solvent during microscope sample preparation. In contrast, the latex sample that had been destabilized by treatment with air and heat showed extensive aggregation, producing particles that are much larger than 1 $\mu$m. It is important to note that the primary particles, while they are touching each other in the aggregates, remain spherical and do not fuse together.

## CONCLUSION

Switchable long chain alkyl amidine surfactants can be used to stabilize emulsions of styrene and methyl methacrylate. Emulsion polymerization conducted using an azo-based free radical initiator yields stable colloidal polymer latexes with controllable particle sizes ranging from 41 to 372 nm. The latex samples are stable as long as they are saturated with $CO_2$.

Treatment of latexes stabilized by surfactants such as **2a** and **2b** with heat and air, Ar, or $N_2$ results in the formation of micrometer-sized polymer aggregates that can be readily separated from the aqueous phase. This destabilization procedure does not involve the addition of copious amounts of salts or strong acid and thus has the dual benefit of not contaminating the water (which would then subsequently need further purification) or the product (which could alter its final properties). The use of air and heat rather than salt or acid in the destabilization of latex samples could reduce the environmental impact of latex processing.

The aggregation behavior of polystyrene and poly(methyl methacrylate) latexes depends heavily on the amount of surfactant and initiator in the system, as well as the polymer concentration, with more surface amidine groups and higher polymer concentrations resulting in a higher volume fraction of aggregates at a fixed time of 5 h. The final size of the polymer aggregates depends on the choice of monomer (styrene versus MMA) and the polymer concentration (in the case of polystyrene).

Because these switchable surfactants are known to be able to undergo multiple switching cycles, redispersion of the destabilized polymer aggregates by reintroducing carbon dioxide should be possible. This would create polymer particles that can be reversibly stabilized, which will be the subject of a forthcoming paper.

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