

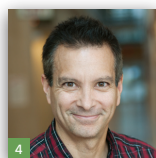
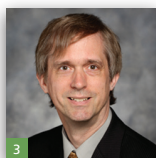
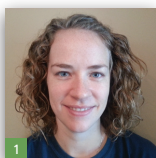
Redispersing aggregated latexes made with switchable surfactants

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Amidine-based switchable surfactants can be used as stabilizers during emulsion polymerization, and the resulting latexes can then be destabilized simply by the removal of CO₂. Polystyrene and poly(methyl methacrylate [MMA]) latexes have been successfully redispersed by reintroducing CO₂ to the latex, as shown by recovery of primary particle size, but an input of energy was required. Sonication is the most effective method of energy input, but lower-energy methods, such as rotor–stators and a blender, are successful in redispersing some aggregated latexes. Colloidal stability was found to be reversible for at least three aggregation/redispersion cycles, and redispersibility was achieved even after the removal of water and addition of fresh water. The traditional method of aggregating latexes involves addition of salts, acids or bases, which result in a contaminated wastewater stream. Furthermore, aggregated latexes cannot usually be redispersed. This approach could enable dewatering of latexes prior to transport followed by redispersion at the point of use, yielding significantly reduced transportation costs and energy consumption.

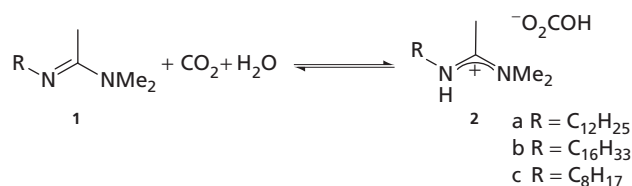
1. Introduction

Emulsion polymerization is used to produce many different types of polymer colloids. In addition to its economic advantages over most solution and bulk polymerization processes, it is also an environmentally attractive process because of the usage of water in the continuous phase. However, for applications where recovery of the polymer in resin form is required, large amounts of salts, acids or bases are used to destabilize the latexes. With salts, the increase in ionic strength causes a collapse in the electrical double layer, which causes aggregation of the polymer particles.¹ For latexes stabilized (all or in part) by weak acid or base moieties, neutralization by addition of base or acid induces aggregation. The large amount of destabilizing chemicals then need to be cleaned from the final product, creating additional purification costs and environmental impact.

By using switchable surfactants during emulsion polymerization, it is possible to produce a colloidal system with switchable stability.

Switchable surfactants are surfactants that can undergo reversible interconversions between active and inactive forms; a trigger is used to switch between the two states. This trigger can be a redox process as in the ferrocene-, viologen- and pyrazinium-based switchable surfactants^{2–4} or photochemical as in the reversible switch of azobenzene surfactants.⁵ The authors have reported switchable surfactants based on long-chain acetamidines; CO₂ is the trigger used to convert the surfactant into its active form, whereas argon or air (or any nonacidic gas) are used to switch the surfactant into its inactive form by removing the CO₂. Amidines show this reversibility by becoming bicarbonate salts when exposed to the CO₂. Scheme 1 shows the reversible reaction between the amidine and CO₂.⁶ The use of these switchable surfactants in emulsion polymerization has recently been reported by our group.⁷ Latexes with good colloidal stability can be produced using a switchable surfactant and switchable free radical initiator. These latexes can then be aggregated with the removal of CO₂ by heating and bubbling with an inert gas.

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Scheme 1. The reversible reaction between an amidine and CO_2 or air and heat where compound **2** is the active surfactant.

Stimuli-responsive polymer colloids with reversible colloidal stability may have many uses. For example, transportation costs could be dramatically reduced if it were possible to dewater a latex, ship the concentrated polymer particles and then reintroduce water and redispersed the particles at the desired location where the latex is to be used. Redispersible latexes have been reported, but in most cases require the addition of acids or bases.^{8–10} Guziak *et al.*⁸ reported preparing a latex with at least 10 wt% carboxylic acid-containing monomer (methacrylic acid). The latex was dried to a granular free-flowing solid and redispersed by adding water and a base. The reconstituted latex, once dried again, was not redispersible for a second time. Saija *et al.*⁹ also reported the use of acidic groups to produce a redispersible polymer. Latexes were dried, and water was reintroduced along with a strong base to redisperse. By using stronger acid groups during polymerization, redispersion was possible at lower pH. Greene *et al.*¹¹ also made use of acidic surface groups for redispersion. No base was required to redisperse the dried latex, but instead 2 min of blending with a Waring blender was needed. The use of a polyvinyl alcohol (PVA) membrane as a protective colloid to produce a redispersible film has also been reported.¹² The PVA shields the particles from each other and keeps them separated during film drying making it possible to redisperse when water is reintroduced. Another pH sensitive example is the use of macroazoinitiators to form switchable “hairy” latex particles.¹⁰ Base was added to induce aggregation, and the reconstituted latex was obtained when lowering the pH again. The reversibility was only possible for three cycles before salt-induced aggregation occurred.

Another method to produce switchable latex particles is to chemically bind switchable groups to the surface of the particle by the copolymerization of a small (switchable) molecule and a monomer. Zhu *et al.*¹³ functionalized a polystyrene particle with a switchable amidine group by copolymerization. To match the reactivities of styrene and their switchable comonomer, they functionalized the phenyl ring in styrene with the switchable group to form the comonomer. They performed the emulsion polymerization surfactant-free and obtained particles with switchable colloidal stability. However, their system did not undergo aggregation with the application of air and heat, most likely due to their poor choice of initiator; the HCl contained therein would protonate their switchable amidine groups and not be removable by air and heat.

A recent publication from our group discussed the redispersion of aggregated latexes prepared with amidine based switchable

surfactants.¹⁴ The amidine-switchable surfactants as well as a switchable initiator were used to prepare the latexes. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] (VA-061) is an azo-based initiator that contains two imidazoline groups, which when in carbonated water become protonated and form a bicarbonate salt. The initiator group, which becomes chemically bound to the particle surface, also helps with switching along with the surfactant. It was found that latexes were only switchable by addition and removal of CO_2 if both switchable surfactant and switchable initiator were used. If a switchable molecule (surfactant or initiator) was used in conjunction with a nonswitchable molecule, switchability was lost. The redispersions were carried out on polystyrene latexes prepared with large amounts of switchable groups. The amount of switchable initiator ranged between 1 and 10 mol%, and 1.5 mol% of switchable surfactant was used. This is a much larger amount of initiator used compared with the amount used in the present article. Furthermore, in this article, it will be shown that significantly less time is required for the redispersion process.

The emphasis of this article is on the redispersion of aggregated polymer particles prepared with an amidine-switchable surfactant. The author demonstrate that switchability can be achieved with much lower concentrations of switchable surfactant and initiator compared with previous results. The switchable latexes exhibit reversible aggregation/redispersion through multiple switching cycles. The authors also examined alternative and more industrially practical methods of energy input used to facilitate redispersion.

2. Experimental

2.1 Materials

2,2'-Azobis[2-(2-imidazolin-2-yl)propane] (VA-061) and 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and cetyl trimethylammonium bromide (CTAB, 98%) from Aldrich were used without further purification. MMA (99%) from Aldrich, containing 4-*tert*-butylcatechol (10–15 ppm) as the inhibitor, was purified by being passed through an inhibitor removal column (Aldrich). N'-Dodecyl-N,N-dimethylacetaminidinium bicarbonate (**2a**, hereafter referred to as C12) was prepared according to the previously reported procedure.⁶ Medical grade CO_2 from Praxair (Canada) and distilled deionized water were used in all experiments. Disponil A 3065®, a 30 wt% mixture of nonionic surfactants from Cognis (Canada), was used after dilution to 1 wt%.

2.2 General emulsion polymerization procedure

Carbon dioxide was bubbled through distilled water (60 mL) in a round bottom flask with a needle for 30 min to carbonate the water. Meanwhile, C12 (0.12 mol% with respect to MMA) was dissolved in MMA (31.3 mmol) with the help of sonication. The monomer-surfactant mixture was added to the carbonated water and allowed to stir for 30 min to create a stable emulsion. During that time, a

portion (~5 mL) of the previously carbonated water was added to VA-061 (0.07 mol%, with respect to MMA) to create a solution of the bicarbonate salt of the initiator. The round bottom flask was then equipped with a condenser, and the initiator solution was added. The polymerization was performed at 65°C, while maintaining bubbling with CO₂ and stirring to ensure saturation of the aqueous phase with CO₂ (excess CO₂ relative to amidine groups). The reaction was allowed to proceed for 5 h before the flask was removed from the heat. The resulting latex had a solid content of 5 wt% that was measured gravimetrically. Monomer conversion was typically between 80–95%, which was also determined gravimetrically.

2.3 Emulsion polymerization of a latex containing no switchable groups

For a control sample, a latex was prepared with no switchable groups. In order to achieve this, the same procedure was followed as mentioned earlier, but the surfactant and initiator were CTAB and VA-044, respectively. Argon rather than CO₂ was sparged through the system.

2.4 Aggregation

Aggregation of the control sample was accomplished by adding salt (0.1 g of Al₂(SO₄)₃) to increase the ionic strength and cause destabilization. The aggregated latex was centrifuged for 10 min at 3500 rpm to decant the supernatant. Fresh water (~20 mL) was added to the sample, which was centrifuged again at the same conditions. The supernatant was decanted to remove the salt. Finally, fresh water (~20 mL) was added to yield a solids content of 3.4 wt%.

Aggregation of latexes prepared with the switchable surfactant and initiator was achieved by sparging with air at 80°C until the particle size increased (this was generally determined visually by an increase in viscosity, before the particle size was measured). The aggregation time ranged between 2.5 and 24 h, depending on the volume of latex that was being destabilized.

2.5 Redispersion

Redispersion was attempted using four different energy-input methods, as described below. For all redispersion methods, some samples were exposed to CO₂ after redispersion by bubbling with a needle for 10 min and some were not. All redispersions were performed at room temperature. After the particle sizes and zeta potentials of the redispersed samples were measured, all vials were capped and sealed with Parafilm® (USA). Proper sealing of vessels is necessary to prevent the escape of CO₂, which would cause latex destabilization.

- (a) Probe sonicator: an Omni Sonic Ruptor 250 W Ultrasonic Homogenizer, equipped with a 3/8" titanium processing tip (Omni International, USA) was placed approximately 1.5 cm into 20 mL of an aggregated latex in a 35-mL vial. The probe power was set to 10%, and the sample was sonicated for 1 min.

- (b) Rotor–stator: an aggregated latex (500 mL) was redispersed in a vessel, with a condenser jacket to prevent over heating, using a VMI Rayneri TURBOTEST rotor–stator, with a diameter of 5.5 cm, at 2500 rpm for 1 min.

- (c) A hand-held blender: approximately 200 mL of aggregated latex was placed in a tall (30 cm) plastic container. A Lancaster 1-Speed Hand Blender (purchased from Canadian Tire, Canada) was immersed into the aggregated latex so that the blade was approximately 3 cm from the bottom of the vessel and was turned on for 1 min of blending. The samples were not cooled during redispersion and the temperature increased only slightly after agitation.

- (d) An overhead stirrer: approximately 80 mL of aggregated latex was put in a 150-mL tall-form Berzelius beaker, and an IKA Power Control-Visc overhead stirrer (130 W) equipped with an IKA R2305 four-blade propeller was used for redispersion. The four-blade stirring probe was placed approximately 1 cm above the bottom of the beaker and the aggregated latex was stirred at 900 rpm for 1 min.

2.6 Characterization

Particle sizes and zeta potentials of latexes were measured using dynamic light scattering with a Zetasizer Nano ZS (Malvern). Each measurement was the average of five individual measurements. The particle sizes of aggregated latexes and the redispersed latexes were measured using static light scattering with a Malvern Mastersizer 2000 (Malvern) equipped with a Hydro2000S optical unit. Use of the Mastersizer 2000 requires significant dilution of the sample; because of this, a nonionic surfactant, Disponil A 3065® (0.5 wt%, with respect to mass of latex), was added to the sample immediately before a measurement to prevent further aggregation within the instrument.

3. Results and discussion

It is not necessary to use switchable surfactants or switchable initiators to create a latex that can be aggregated and then redispersed, but the aggregation step of such a latex requires the addition of a significant concentration of a salt. For example, a 5 wt% polymethylmethacrylate (PMMA) latex, prepared by emulsion polymerization with a nonswitchable surfactant (0.12 mol% CTAB) and a nonswitchable initiator (0.07 mol% VA-044), had a particle size of 80 nm and a zeta potential of 45 mV. The latex (6 g) cannot be aggregated with air and heat but can be aggregated by salt addition (0.1-g aluminium sulfate), producing a particle size of 7 µm. The redispersion of this aggregated latex was then attempted using a sonicator probe, with or without prior washing of the sample. Table 1 shows the results of the redispersion attempts, including the volume % of particles below 1 µm and the zeta potential of the redispersed control samples immediately after redispersion and 7 days later. The unwashed aggregated

	No washing		Washed	
	Vol. % <1 μm (particle size)	Zeta potential (mV) ^a	Vol. % <1 μm (particle size)	Zeta potential (mV) ^a
Immediately after redispersion	92.1 (154 nm)	26 \pm 1	100 (121 nm)	30 \pm 1
Seven days later	0 (5.1 μm)	25 \pm 3	97.9 (126 nm)	28 \pm 1

Redispersion by sonicator probe for 1 min at a setting of 10%. The original sample was a 5 wt% latex prepared with 0.12 mol% CTAB and 0.07 mol% VA-044 with an initial particle size of 80 ± 1 nm and zeta potential of 45 ± 1 mV which was aggregated, by addition of aluminium sulfate, to 7.2 μm (not washed) and 10.5 μm (washed).

^aThe error in zeta potential is the standard deviation from the five measurements that are taken for one sample.

Table 1. Redispersion by sonication of a PMMA latex that was aggregated by the addition of aluminium sulfate.

control sample was redispersed after 1 min of sonication, resulting in 133-nm particles. However, the latex was not stable and reaggregated to give large particles. The washed control sample showed good redispersion after sonication and had a slightly higher zeta potential. After 7 days, the washed control sample still showed only slightly degraded colloidal stability. From these results, it seems that while redispersion of a 5 wt% latex aggregated with salt is possible, it does not have long-term colloidal stability unless the aggregated sample is washed sufficiently to remove the salt.

In contrast, a latex prepared with a switchable surfactant and a switchable initiator can be aggregated without the addition of a salt and then redispersed without the washing step. Poly(methyl methacrylate) latex samples were prepared by emulsion polymerization using the switchable surfactant, C12 and the switchable initiator, VA-061. The latex samples had a monomodal distribution ($d_v = 120$ nm, Figure 1). These latexes were then aggregated with air and heat (80°C). The resulting aggregates had a monomodal distribution with $d_v = 8.7$ μm . The small peak at approximately 110 μm in the aggregated latex distribution is not due to particles, but is due to air bubbles in the instrument. Introducing CO_2 to switch the surfactant back to its active form was not sufficient on its own to redisperse the aggregated latexes; additional energy was needed to induce redispersion. After redispersion, nearly the original particle size is obtained ($d_v = 138$ nm). Figure 1 shows a typical particle size distribution plot based on volume distribution.

Redispersion of these switchable latexes may be assisted by residual surface charge remaining after the aggregation step. After the aggregation of the latex with heat and air, the switchable surfactant should be in its neutral (“off”) form, which means that there should be no active surfactant in the system. However, the authors observed that the zeta potential did not decrease to zero or near-zero, indicating that there was residual surface charge and therefore that there were still some surfactants or initiator end groups in their “on” form. While the amidine surfactants can be switched nearly completely “off” in homogeneous solutions,

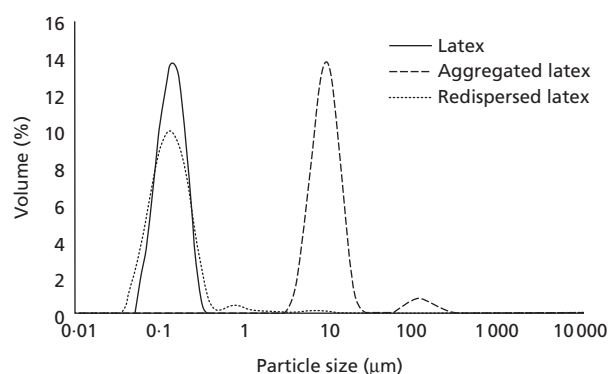






Figure 1. Particle size distributions of a latex after preparation ($d_v = 120$ nm), after aggregation (with air at 80°C, $d_v = 8.7$ μm) and after redispersion (sonication with a probe sonicator for 1 min, $d_v = 138$ nm). The 5 wt% original latex contained 0.12 mol% C12 surfactant and 0.07 mol% VA-061. Distributions were measured using static light scattering. The peak at 110 μm is due to bubbles.

the authors have consistently seen postaggregation zeta potentials of ~ 20 mV for latex particles. This behavior is currently being investigated further. The authors speculate that if the zeta potential had been fully reduced to zero during the aggregation process, subsequent redispersion might have been considerably more difficult.

The method of introducing the energy for redispersion determines the stability and particle size of the redispersed latex. Table 2 compares the effectiveness of different redispersion methods with and without the presence of CO_2 for the redispersion of 5 wt% latexes that had been aggregated with air at 80°C. In the absence of CO_2 , the sonicator, rotor–stator and blender were all successful in redispersing the 5 wt% aggregated latex. The overhead stirrer, however, did not provide enough shear to induce redispersion. Even after 7 days, the sonicator- and blender-dispersed samples were still stable, but the sample dispersed with the rotor–stator reaggregated. The authors believe that the reaggregation was due to incomplete redispersion of the sample; the remaining population of larger particles would have promoted

			Method			
			Sonication ^a	Rotor-stator ^b	Blender ^c	Stirrer ^c
						
No CO ₂ exposure	Immediately after redispersion	Vol. % <1 µm (particle size)	99.7 (123 nm)	60.4 (166 nm and 3.5 µm)	98.6 (123 nm)	0 (9.7 µm)
		Zeta potential (mV)	19 ± 1	13 ± 6	19 ± 2	21 ± 2
	Seven days after redispersion	Vol. % <1 µm (particle size)	98.8 (126 nm)	0 (3.8 µm)	99.7 (123 nm)	0 (9.6 µm)
		Zeta potential (mV)	20 ± 1	5 ± 1 ^d	19 ± 1	19 ± 2
CO ₂ exposure	Immediately after redispersion	Vol. % <1 µm (particle size)	99.8 (128 nm)	64.9 (173 nm and 3.1 µm)	98.4 (124 nm)	0 (8.9 µm)
		Zeta potential (mV)	22 ± 1	14 ± 1	22 ± 2	23 ± 1
	Seven days after redispersion	Vol. % <1 µm (particle size)	99.8 (123 nm)	65.8 (171 nm and 3.4 µm)	98.2 (124 nm)	0 (9.4 µm)
		Zeta potential (mV)	27 ± 2	22 ± 2	29 ± 2	27 ± 1

All latexes were made with 0.12 mol% C12 and 0.07 mol% VA-061 and destabilized with air at 80°C.

^aThe original latex with primary particle size of 132 ± 1 nm and zeta potential of 43 ± 1 mV, and aggregated to 8.0 µm with a zeta potential of 20 ± 1 mV.

^bThe original latex with primary particle size of 128 ± 1 nm and zeta potential of 38 ± 1 mV, and aggregated to 7.2 µm with a zeta potential of 18 ± 2 mV.

^cThe original latex with primary particle size of 124 ± 2 nm and zeta potential of 46 ± 3 mV, and aggregated to 8.9 µm with a zeta potential of 20 ± 1 mV.

^dSample separation occurred in the capillary cuvette during measurement.

Table 2. The redispersion of a 5 wt% aggregated PMMA latex containing with different methods of agitation in the presence and absence of CO₂.

aggregation of the smaller particles because the total interaction energy between a small and a big particle is larger than that between two small particles. The stability of the sonicator- and blender-dispersed samples was somewhat unexpected because of the presumed

absence of active surfactant but can likely be attributed to the residual surface charge. Furthermore, the low solids content means that particle collisions are infrequent. The following equation shows the relationship between aggregation half-life, $t_{1/2}$, and solids content, ϕ :

$$1. \quad t_{\frac{1}{2}} = \frac{\pi \eta d^3}{8kT\phi}$$

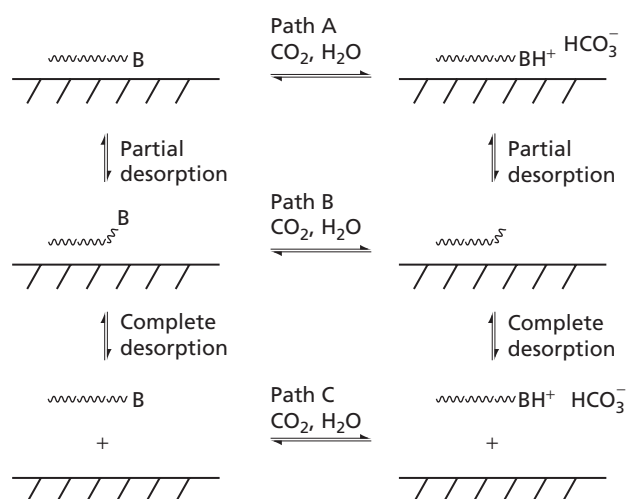


Figure 2. Three possible pathways for the reprotonation of an amidine-switchable surfactant that is adsorbed to the latex particle surface. “B” represents the basic amidine headgroup in its neutral form.

where η is the viscosity of the medium, d is the particle diameter, k is Boltzmann’s constant and T is the temperature.¹⁵ This inverse relationship shows that with lower solids content the time required for particle aggregation increases. Hence, the latexes with only 5 wt% solids would be kinetically stable for some time at room temperature, even with a low zeta potential.

Samples that were exposed to CO₂ also resulted in successful redispersion, although the rotor–stator only gave partial redispersion, and the overhead stirrer was again incapable of redispersing the sample. On exposure to CO₂, the surfactant should switch back to its charged form, and correspondingly the surface charge should increase resulting in a higher zeta potential. However, the zeta potentials of the CO₂-exposed samples increased only slowly after redispersion, implying that the surfactant did not immediately switch back on. After 7 days, the zeta potentials did increase, and the samples retained colloidal stability. The fact that the rise in zeta potential with time is slow suggesting that the reaction of the amidine with CO₂ is slow, even though the authors know from prior experience that the reaction of acetamidines with CO₂ in water normally takes only minutes. It is possible that the slow step is not the reaction in water but rather the dissociation of the amidine headgroup from the surface. If the amidine headgroup of the “off” surfactant lies flush with the surface of the particle, then the local environment around that headgroup should be fairly low in polarity, which is not favorable for the conversion of the amidine to the bicarbonate salt (path A of Figure 2). If, however, the amidine

headgroup was some distance from the surface and therefore in a primarily aqueous environment, then the salt formation could take place readily. This movement of the amidine group into the aqueous environment could be caused by either complete desorption of the amidine molecule from the surface or desorption of only the head group, while the hydrophobic tail stays adsorbed to the surface (paths B and C of Figure 2). Diffusion of the amidine group from the surface may be slow, thereby retarding the switching on process. It is also possible that absorption of neutral amidine into the PMMA particle occurs during or after the aggregation process, which would affect the rate at which the zeta potential can increase after redispersion. The authors expect the surfactant to have a solubility parameter near to those of tributylamine (15.8 MPa^{1/2}) and dodecane (16.2 MPa^{1/2}), placing the surfactant between ether and tetrahydrofuran (THF) on a solubility scale. PMMA is soluble in THF but not in ether, so it is probable that the surfactant has some limited solubility in PMMA. Any absorbed surfactant would not be in contact with the water phase to be protonated by CO₂, thereby resulting in less surface charge (lower zeta potential). However, slow migration of absorbed surfactant to the surface followed by protonation could be responsible for the slow increase in zeta potential. It is not known at present whether migration of absorbed surfactant to the surface or the desorption of adsorbed surfactant is responsible for the slowly increasing zeta potential.

Redispersion of latexes having a higher solids content is a more challenging task. With a higher concentration of particles, aggregation due to Brownian motion occurs more quickly. When redispersion was attempted with latexes having 15 wt% solids content, redispersion was not possible in the absence of CO₂ (Table 3). With all four methods, primary particle sizes were not obtained. Even in the presence of CO₂, redispersion was unsuccessful with the rotor–stator, blender and overhead stirrer. The particle size of the sample treated with the rotor–stator could not be measured because the sample was turned into a thick foam due to air entrapment. Redispersion was successful only with sonication in combination with CO₂. If the sample was exposed to CO₂ for 5 min and then sonicated for 1 min, followed by CO₂ bubbling for another 10 min, then the zeta potential immediately after the treatment increased from 24 to 31 mV. This sample was monitored over 3 weeks, and it maintained its stability and high zeta potential (Table 4). If CO₂ exposure was performed after sonication, redispersion was ineffective, which is evidence that CO₂ is required for successful redispersion.

Now that a single successful aggregation/redispersion cycle has been demonstrated, an important question is whether the aggregation/redispersion cycle is repeatable. As mentioned in the introduction, redispersible polymers reported in the literature have limited aggregation/redispersion cycles, sometimes because of the accumulation of salts formed by the acid and base triggers. Because CO₂ addition and removal is the trigger for the switchable surfactant, there is no accumulation of salts and consequently

			Method			
			Sonication ^a	Rotor–stator ^b	Blender ^a	Stirrer ^b
No CO ₂ exposure	Immediately after redispersion	Vol. % <1 µm (particle size)	0 (5.4 µm)	0 (5.5 µm)	0 (5.6 µm)	0 (7.5 µm)
		Zeta potential (mV)	18 ± 1	16 ± 1	21 ± 1	19 ± 2
	Seven days after redispersion	Vol. % <1 µm (particle size)	0 (5.3 µm)	0 (5.9 µm)	0 (5.3 µm)	0 (7.8 µm)
		Zeta potential (mV)	20 ± 1	–	19 ± 1	16 ± 1
CO ₂ exposure	Immediately after redispersion	Vol. % <1 µm (particle size)	98.2 (125 nm)	–	0 (5.0 µm)	0 (7.8 µm)
		Zeta potential (mV)	31 ± 2	–	24 ± 2	18 ± 1
	Seven days after redispersion	Vol. % <1 µm (particle size)	98.0 (127 nm)	–	0 (5.1 µm)	0 (7.6 µm)
		Zeta potential (mV)	29 ± 1	–	29 ± 1	20 ± 1

All latexes were made with 0.12 mol% C12 and 0.07 mol% VA-061 and destabilized with air at 80°C.

^aThe original latex with primary particle size of 107 ± 2 nm and zeta potential of 46 ± 2 mV, and aggregated to 8.4 µm with a zeta potential of 24 ± 1 mV.

^bThe original latex with primary particle size of 139 ± 2 nm and zeta potential of 40 ± 3 mV, and aggregated to 8.1 µm with a zeta potential of 17 ± 1 mV.

Table 3. The redispersion of a 15 wt% aggregated PMMA latex with different methods of agitation in the presence and absence of CO₂.

Time (days)	Vol. % <1 µm (particle size)	Zeta potential (mV)
0	98.2 (125 nm)	31 ± 2
7	98.0 (127 nm)	29 ± 1
14	96.4 (130 nm)	32 ± 1
21	97.4 (131 nm)	32 ± 2

The original latex was made with 0.12 mol% C12 and 0.07 mol% VA-061. The latex had a primary particle size of 107 ± 2 nm and a zeta potential of 46 ± 2 mV and was aggregated to 8.4 µm with a zeta potential of 24 ± 1 mV.

Table 4. Long-term colloidal stability of a 15 wt% aggregated PMMA latex after redispersion with sonication and CO₂.

Treatment	Vol. % <1 µm (particle size)	Zeta potential (mV)
None (original latex)	100 (124 nm)	46 ± 3
Air and heat	0 (8.9 µm)	20 ± 1
Sonication and CO ₂	100 (120 nm)	19 ± 1
Air and heat	0 (8.3 µm)	13 ± 1
Sonication and CO ₂	93.9 (133 nm)	15 ± 1
Air and heat	0 (6.0 µm)	13 ± 1
Sonication and CO ₂	100 (122 nm)	18 ± 1

The original latex was made with 0.12 mol% C12 and 0.07 mol% VA-061. To aggregate, samples were bubbled with air and heated at 80°C. To redisperse, samples were sonicated for 1 min at 10% power and bubbled with CO₂ for 10 min

Table 5. Multiple cycles of aggregation and redispersion of a 5 wt% PMMA latex.

	No CO ₂ exposure		CO ₂ exposure	
	Vol.% <1 µm (particle size)	Zeta potential (mV)	Vol.% <1 µm (particle size)	Zeta potential (mV)
Immediately after redispersion	99.0 (122 nm)	18 ± 1	97.9 (127 nm)	18 ± 1
Seven days later	98.7 (123 nm)	16 ± 1	97.8 (123 nm)	17 ± 1

Table 6. Redispersion of a rehydrated 4.9 wt% aggregated latex with 0.12 mol% C12 and 0.07 mol% VA-061.

the switch should, in theory, be possible for multiple cycles. Three aggregation/redispersion cycles were performed on a 5 wt% latex (Table 5). The sample was aggregated with air and heat (80°C) and redispersed with sonication for 1 min and 10 min of CO₂ bubbling. As expected, the first aggregation step with air and heat led to all particles being over 1 µm and having a zeta potential of 20 mV. The zeta potential after the first redispersion step was almost the same, this was expected because previous experiments (Table 2) showed that it takes 7 days for the zeta potential to increase. The second and third aggregation steps again resulted in complete conversion to particles greater than 1 µm and increased the zeta potential relative to that after aggregation.

If switchable latexes of this type were to be used for transportation, it would be useful to be able to remove some of the water from the aggregated material to reduce shipping costs. The authors therefore tested whether this could be done while retaining redispersibility. A 4.6 wt% aggregated PMMA latex was prepared with 0.12 mol% C12 and 0.07 mol% VA-061 to give a primary particle size of 124 ± 2 nm and a zeta potential of 49 ± 3 mV. The latex was aggregated with air at 80°C to give a particle size of 9 µm with a zeta potential of 20 ± 1 mV. The aggregated latex (40 mL) was filtered by suction filtration using a fine frit, removing 30 mL of water to give a solids content of 18 wt%. Fresh deionized water was added to obtain a 4.9 wt% rehydrated aggregated latex. Some of the rehydrated sample was then sonicated for 1 min at 10% power without CO₂. Another portion of the sample was exposed to CO₂ for 5 min, then sonicated for 1 min at 10% power, followed by further CO₂ bubbling for 10 min. Table 6 shows the volume % below 1 µm and the zeta potentials of the redispersed samples immediately after redispersion and 1 week later. The samples were successfully redispersed using either redispersion method, indicating that the removal of water does not affect the redispersibility of the latexes.

4. Conclusions

The redispersion of aggregated latexes made by emulsion polymerization using switchable surfactants triggered by CO₂ has been shown to be successful, with the primary particle size of the latexes obtained after redispersion. The concentrations of switchable surfactant and initiator required to produce reversibly

switchable latexes is much lower than has been previously reported. Redispersion requires energy input and sonication, which has been used previously, is not easily scalable. Alternative scalable methods (rotor–stator and immersion blender) were able to redisperse a 5 wt% aggregated latex. An overhead stirrer (four-blade propeller) did not induce redispersion. Low polymer concentration samples (5 wt%) were stable for several weeks with or without CO₂ atmosphere.

Samples with higher polymer concentration (15 wt%) were more difficult to redisperse. Only the sonicator probe supplied sufficient energy to completely redisperse the samples. In this case, the presence of CO₂ was necessary for successful redispersion.

The switchable latexes were shown to be reversible for at least three aggregation/redispersion cycles. Because the trigger for switching of the surfactant is the addition and removal of CO₂ rather than the addition of acid and then base, and there is no salt accumulation and therefore no inherent reason that the system should have a limited number of cycles.

Acknowledgements

The authors thank the Xerox Research Center of Canada for continued support and advice, the National Sciences and Engineering Research Council, the Ontario Research Chairs Program (for MFC) and the Canada Research Chairs Program (for PGJ) for financial support.

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