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Redispersible Polymer Colloids Using Carbon Dioxide as an External Trigger

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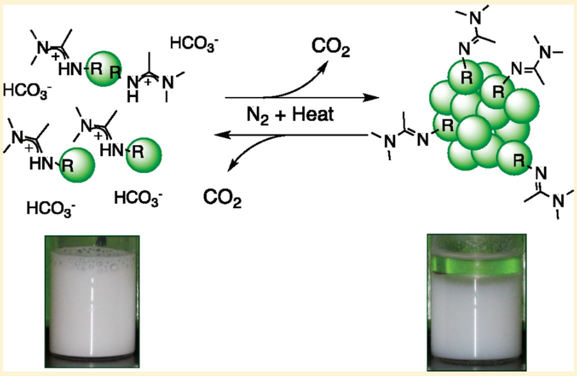
ABSTRACT: Polystyrene latexes prepared using a carbon dioxide switchable amidine surfactant and a switchable free radical initiator can be aggregated using only nitrogen and gentle heat and redispersed using carbon dioxide and sonication. The long-term colloidal stability of the redispersed latexes is excellent provided they are maintained under a carbon dioxide atmosphere. Redispersion of the particles is most effective when both the surfactant and the initiator contain switchable amidine moieties. The zeta potential of the original particles (with the switchable surfactant/initiator in their active form) decreases when the surfactant and initiator are converted to their inactive form upon addition of nitrogen and heat. Zeta potential is restored to its original value upon conversion of the surfactant and initiator to their active forms with carbon dioxide addition. This is the first report of redispersible polymer colloids that can be aggregated by reduction of surface charge, without requiring added acid or base solution. These switchable latexes demonstrate the future potential for switchable polymer colloids, capable of undergoing multiple reversible aggregation—redispersion cycles.



INTRODUCTION

Emulsion polymerization is an industrially important process used to manufacture a variety of polymer colloids for numerous applications such as coatings, adhesives, binders, and paints. It is also increasingly being used for preparing particles with tailored functionality, microstructure, or morphology for more specialized applications. Control of the colloidal stability is essential for all of these applications. The traditional approach is to ensure that excellent colloidal stability is maintained both during polymerization and in the post-reaction states (e.g., storage, transportation). However the development of redispersible polymer colloids is of significant interest from scientific and technology perspectives, particularly if the particles could be made stimuli-responsive so that the properties and stability of the colloidal suspension could be reversibly switched. The synthesis and design of stimuli-responsive polymers are stimulating extensive research because of a variety of applications. Reversible changes in chemical or physical properties in response to an external trigger such as temperature, pH, or, in our system, carbon dioxide may enable the design of new materials in fields including material science, nanotechnology, and biomedicine. Larger scale applications for redispersible polymer colloids are also possible. For example, if an aggregated polymer latex could be dewatered, then transported (containing only a minimum amount of water), and finally redispersed with addition of water at its destination, there would be dramatic savings in energy and transportation costs.

Stabilization of polymeric dispersions is achieved through the presence of surfactants that preferentially locate at the interface between the particle and the continuous phase. The features that make a surfactant effective (i.e., preservation of excellent colloidal stability during polymerization and later storage) also make it a challenge to "break" (coagulate/aggregate) the dispersion. Destabilizing the dispersion usually requires the addition of chemicals (e.g., salt, acid, or base) to the dispersion; the added chemicals are usually undesirable in the final product, and additional processing steps are required to remove them, a step that also results in an additional waste steam.

However, it is very difficult to achieve reversible interconversion from uniformly suspended polymer particles in an aqueous medium to an aggregated state comprising polymer particles and clear liquid. Although redispersible polymer colloids have been reported,[1−6] they generally require further additives, including an acid or base, to facilitate redispersion. Earlier studies on redispersible latexes were often motivated by concerns about poor film formation and the desire to understand conditions under which dried films were prone to redispersion upon exposure to water.[1−4] Latexes with very high concentrations of surface carboxylic acid groups and high pH may undergo redispersion after being dried to a film and then mixed in water, although high shear (e.g., Waring blender) is required for complete redispersion. The redispersibility is due to the high surface charge, likely coupled with the retention of a hydrated layer at the particle surface. Because the surface charge remains

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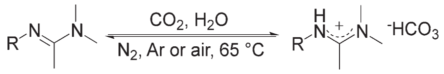
Scheme 1. Amidine Switchable Surfactants in Their “On” (right) and “Off” (left) Forms



high during film drying, such redispersible latexes are not suitable coating materials. “Hairy” polystyrene particles containing a pH-sensitive poly[2-(diethylamino)ethyl methacrylate] surface layer were recently reported.[5] The particles are well dispersed at acidic pH but flocculate in basic media, showing a reversal in charge of zeta potential and increase in mean particle diameter from ∼250 to ∼700 nm. The dispersion−flocculation cycle could be repeated up to three times, with successive acid−base addition, before salt-induced coagulation occurred.

Switchable surfactants are molecules whose surface activity can be reversibly “switched” between inactive and active states by application of a trigger. They offer a potential route to enabling reversible interconversion between an aggregated latex and a well-dispersed colloidally stable latex because they can provide temporary and reversible stabilization of an emulsion or suspension. A few switchable surfactants have been developed but often with economically or environmentally undesirable triggering agents. Some of these are based upon oxidation/reduction cycles[8,9] or acid/base cycles[10] which produce undesirable waste. Photochemical[11,12] or photoelectrochemical[13] switches would suffer from photon losses due to liquid phase opacity in emulsions and suspensions. We previously reported in a brief communication that long-chain alkylamidine compounds can be reversibly transformed into cationic surfactants (amidinium bicarbonates) by exposure to an atmosphere of carbon dioxide (Scheme 1).[7] Among the applications demonstrated was the microsuspension polymerization of styrene to yield polymer particles ∼20 μm in diameter. The microsuspension was readily aggregated by switching off the surfactant through bubbling with argon to remove the carbon dioxide and convert the surface active amidinium bicarbonate back to the inactive amidine.

The application of switchable surfactants to the synthesis and aggregation of nanoscale polymer colloids was only recently reported.[14] However, the redispersion of the latexes was not attempted. The brief communication from our laboratory[7] showed results from one experiment in which large, microsuspension polymer particles (∼20 μm diameter) were made, but that is the only related work in the field of polymeric nanospheres. There have been no previous reports of polymer latexes where aggregation can be induced by reducing surface charge, and then redispersed by restoring the charge, without requiring addition of liquid or solid reagents such as acids or bases. Herein, we report on the preparation of redispersible polymer colloids using nitrogen and carbon dioxide as inexpensive, environmentally benign triggers for the aggregation and redispersion (respectively) of polymer latexes.

EXPERIMENTAL SECTION

Materials. Cetyltrimethylammonium bromide (CTAB) (Aldrich) and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) from Wako Pure Chemical Industries Ltd. (Osaka, Japan) were used without further purification. Styrene (Aldrich) was purified by passing through an inhibitor removal column (Aldrich). *N*′-Dodecyl-*N*,*N*-dimethylacetamidinium bicarbonate (C_{12}-amidine surfactant) was prepared according to our previously reported procedure.[7]

Characterization. Particle size was determined using a Malvern Mastersizer 2000 (size range of 0.05−2000 mm) equipped with a Hydro2000S optical unit and/or a Zetasizer Nano ZS (size range of 0.6−8.9 mm). The choice of instrument depended on the particle size of the sample. The particle size of the original and redispersed latex samples were measured with the Zetasizer Nano ZS. Particle sizes of aggregated latexes were measured with the Mastersizer 2000. Zeta potentials were determined using the Zetasizer Nano ZS. SEM images were recorded on a Hitachi TM-1000. FT-IR spectra were recorded on a Nicolet AVATAR 360 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance-400 (400 MHz, 100 MHz) instrument. Styrene conversion was determined gravimetrically. A Carousel 12 Reaction Station (R. B. Radley Co. Ltd.) was used as a reactor for the emulsion polymerizations. A Fisher Scientific Model FS30 was used as a sonicator for redispersion of the aggregated latexes.

Emulsion Polymerization of Styrene Using CTAB and VA-044. A mixture of CTAB (1.5 mol %, with respect to styrene), styrene (20 mmol), and distilled water (7 mL) was placed in a glass tube and then stirred with bubbling nitrogen for 30 min at room temperature. To the mixture, VA-044 (5 mol % with respect to styrene) in water (3 mL) was slowly added and then stirred with bubbling nitrogen for 30 min. The reaction mixture was heated at 65 °C for 5 h in the Carousel 12 Reaction Station.

General Emulsion Polymerization of Styrene in the Presence of Switchable Surfactant (C_{12}-amidine) and/or Switchable Initiator (VA-061 Bicarbonate, VA-061 BC). The reaction procedure follows the method described above except that C_{12}-amidine surfactant and/or VA-061 bicarbonate were substituted for CTAB or VA-044, respectively, and the reaction mixture was sparged with carbon dioxide instead of nitrogen. All conversions were in the range 85−97%. The VA-061 bicarbonate was prepared immediately prior to use by bubbling carbon dioxide through an aqueous solution of VA-061 and used without isolation.

Procedure for Isolation/Characterization of VA-061 Bicarbonate (VA-061 BC). Carbon dioxide was bubbled through VA-061 (1 mmol) in water (10 mL) until the aqueous solution became transparent. Acetonitrile (10 mL) was added to the solution to yield a white precipitate, which was filtered and then washed with acetonitrile to give 2,2′-(diazene-1,2-diylbis(propane-2,2-diyl))bis(4,5-dihydro-1*H*-imidazol-3-ium) bis(hydrogen carbonate) (VA-061 bicarbonate) as a white solid. The white solid was dried under air. The conversion was 78%. IR (KBr): ν = 3165, 3078, 2933, 2602, 1652, 1632, 1601, 1417, 1283, 978, 834, 703 cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$OD): δ = 1.54 (s, 12 H), 3.94 (s, 8 H). ^{13}C NMR (100 MHz, CD$_3$OD): δ = 23.7, 47.1, 71.5, 161.4, 174.0.

General Procedure for Coagulation of Latex 1 by Bubbling of Nitrogen under Heating. The latex **1** was heated at 65 °C with bubbling of nitrogen for 0.5 h. After water (20 mL) was added, nitrogen bubbling at 65 °C was continued for another 1 h. Additional water (10 mL) was then added to facilitate separation, giving suspension **2**.

Redispersion of Suspension 2d by Sonication. After the treatment of latex **1d** with nitrogen at 65 °C for 1.5 h, the diluted suspension was sonicated for 15 min at 20 °C to give redispersed latex **3d1**.

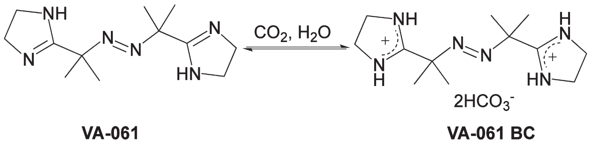
Redispersion of Suspension 2d by Sonication and Carbon Dioxide. The diluted suspension described above was treated using one of two methods. One method involved sonication with bubbling carbon dioxide at 20 °C for 15 min. The other method involved three cycles of sonication at 20 °C for 5 min followed by bubbling of carbon dioxide at room temperature for 5 min.

RESULTS AND DISCUSSION

While studying the behavior of the switchable amidine surfactants, we realized that we could also introduce CO$_2$-triggered

Scheme 2. Structures of the Initiators VA-044 (left) and VA-061 (right)

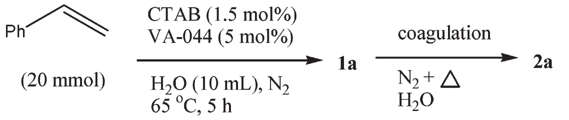
Scheme 3. Preparation of 2,2′-Azobis[2-(2-imidazolin-2-yl)-propane] (VA-061) Bicarbonate (VA-061 BC)



switchable amidine groups onto the polymer chain ends through judicious choice of the free radical initiator, thereby providing an additional source of switchable groups and increased flexibility in the design of switchable latexes. VA-044 and VA-061 are structurally similar initiators, but VA-044 is a dihydrochloride while VA-061 is neutral (Scheme 2). Both have amidine groups, but the VA-044 is not switchable; it remains a salt whether CO_2 is present or absent. However, on the basis of previous experience with amidines, we anticipated that VA-061, an unprotonated amidine, could be converted to a bicarbonate salt by the action of CO_2 and water. This was found to be the case. The bicarbonate salt could be prepared and isolated (Scheme 3), although we found it more convenient to convert VA-061 to the bicarbonate salt *in situ* immediately before a polymerization experiment. We also anticipated that amidinium bicarbonate end groups resulting from polymerizations initiated by the bicarbonate salt of VA-061 would be switchable: they would reversibly lose their charge upon removal of CO_2 from the system.

With both a switchable surfactant and a switchable initiator available, we examined three strategies for making redispersible polymer colloids. The first strategy involves introducing CO_2-triggered switchable groups on the surface of polymer colloids by using a switchable free radical initiator. In emulsion polymerization, ionic initiating species locate primarily (although not exclusively) on the surface of polymer particles. In this approach, a conventional cationic surfactant was used, so that only the initiator-derived end groups on the polymer chains were switchable. The second strategy uses a CO_2-triggered switchable surfactant to provide emulsion stability (with a nonswitchable initiator). The third strategy involves the use of both a CO_2-triggered switchable initiator and a CO_2-triggered switchable surfactant. It will be shown that the best latex redispersibility is obtained when both switchable initiator and switchable surfactant are used together.

Prior to conducting experiments using switchable surfactants or initiators, a control experiment was performed with a nonswitchable surfactant and nonswitchable initiator. The conventional emulsion polymerization of styrene was performed using 1.5 mol % (with respect to styrene) of the surfactant cetyltrimethylammonium bromide (CTAB) and 5.0 mol % of the free radical initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044), whose chemical properties cannot be switched by carbon dioxide (eq 1). The polymerization reached high conversion (96%) within 5 h at 65 °C to give a colloidally stable latex with high zeta potential (particle size: 77 nm; zeta potential: 88 mV). The latex was then treated by sparging with nitrogen at 65 °C. No change in particle size nor zeta potential was observed. The latex was also treated with conventional coagulant. Addition of sodium chloride (500 mg, with 5 mL of water) readily coagulated the latex (1.0 g), giving a mean particle diameter of 16 μm. The particles were then washed with water to remove the residual salt, and more CTAB (0.5 mol %) was added. Sonication for 15 min resulted in only poor redispersion of the latex, with broadly distributed particles ranging from approximately 200 nm to 10 μm (~90 vol % > 1 μm).



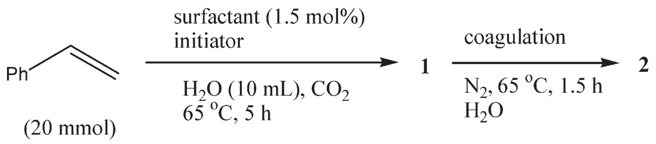
(1)

Latex Synthesis and Aggregation. The three aforementioned strategies were examined to introduce switchability to the latex. Combinations of one surfactant (either switchable or nonswitchable) and one initiator (either switchable or nonswitchable) were tested in styrene emulsion polymerizations (Table 1). 2,2′-Azobis[2-(2-imidazolin-2-yl)propane] bicarbonate, VA-061 BC (Scheme 3), and *N*′-dodecyl-*N,N*-dimethylacetamidinium bicarbonate (C_{12}-amidine surfactant) were used as the CO_2-triggered switchable initiator and the CO_2-triggered switchable surfactant, respectively, in styrene emulsion polymerizations (Table 1). The polymerization yielded stable polymer colloids **1b**−**1f** (Table 1) in the presence of either (a) the nonswitchable surfactant and the switchable initiator (entry 2) or (b) the C_{12}-amidine surfactant and nonswitchable initiator (entry 3). The latexes **1b**−**1f** were then treated by nitrogen sparging and heating at 65 °C (**2b**−**2f**). When only a switchable surfactant or switchable initiator was used, our attempts at coagulation were not effective (entries 2 and 3). In contrast, when the combination of C_{12}-amidine surfactant and 5 mol % VA-061 bicarbonate were used together, coagulation was readily achieved by nitrogen sparging at 65 °C (entry 4). Conversions ranged from 85 to 97%.

The ease and extent of coagulation were affected by the amount of initiator used. The use of 1 mol % of initiator did not give easily coagulated polymer (entry 5), but polymer colloids prepared with 5 and 10 mol % of initiator were easily coagulated with the application of nitrogen and heat (entries 4 and 6).

The improved ease of aggregation when both surfactant and initiator were switchable can be understood in terms of residual charge at the particle surface after the amidinium bicarbonate moieties are switched to amidines. If a permanently charged surfactant (CTAB) or initiator (VA-044) is used, only a portion of the particle surface charge can be neutralized. If both components are switchable, overall surface charge can be dramatically reduced. Although the latexes aggregate, the zeta potential does not decrease to zero, as would be expected if all of the amidinium groups were converted to amidines. Possible reasons include thermodynamic, kinetic, and diffusional limitations on the effective neutralization of the amidinium groups. It is unlikely that diffusional effects alone can account for the observed nonzero zeta potentials, since these values remain essentially constant over periods of days. We are currently exploring this issue further.

Table 1. Emulsion Polymerization of Styrene, Showing Particle Size and Zeta Potential Data before and after Nitrogen Sparging



entry	initiator (mol %)	surfactant (mol %)	1	D_z[a] (nm)	zeta potential (mV)	2	D_z[a] (nm)	D_v[a] (nm)	zeta potential[b] (mV)
1[c]	VA-044 5.0	CTAB 1.5	**1a**	77	88	**2a**	77	101	82
2	VA-061 BC 5.0	CTAB 1.5	**1b**	82	63	**2b**	81	103	66
3	VA-044 5.0	C12 1.5	**1c**	102	85	**2c**	100	112	79
4	VA-061 BC 5.0	C12 1.5	**1d**	84	65	**2d**		43800	34
5	VA-061 BC 1.0	C12 1.5	**1e**	71	49	**2e**	75		34
6	VA-061 BC 10.0	C12 1.5	**1f**	94	60	**2f**		48200	41

[a] D_z and D_v were measured by a Zetasizer ZS and Mastersizer 2000, respectively. [b] Note this is the measured zeta potential of only those particles <30 μm and therefore may not be an accurate measure of the aggregated particles. [c] The emulsion polymerization was carried out under N_2 instead of CO_2.

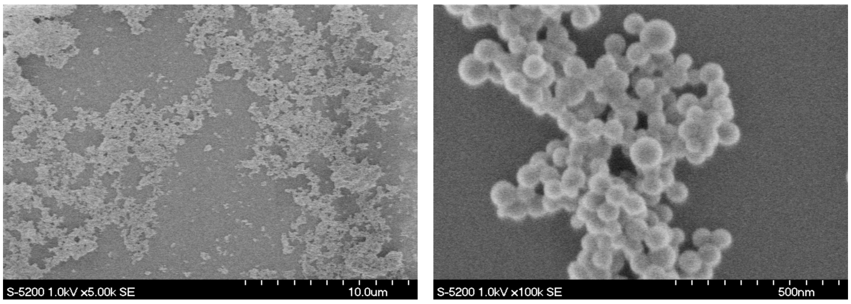


Figure 1. SEM images of aggregated latex **2d**.

These results demonstrate that polymer colloids prepared with CO_2-triggered switchable materials can be aggregated by the application of nitrogen and gentle heat. Although the results are not shown here, argon, air, or other nonacidic gases are also effective in inducing aggregation. The novelty of our approach is not limited to these specific latexes but rather encompasses the concept of inducing switchability in the stability of colloidal particles by using a volatile acid (CO_2) to reduce the particle charge, and any inert gas to restore the particle charge by removing the volatile acid.

SEM images of the coagulated latex **2d** are shown in Figure 1. The polymer **2d** was comprised of large aggregates (10 μm scale image). As shown in the 500 nm scale image, each particle maintained its original spherical shape. Particle size analysis showed that aggregated latex **2d** had a broad particle size distribution, with very few or no particles smaller than 1 μm (Figure 2).

Latex Redispersion. Redispersion of the aggregated latex **2d** was then attempted using three different methods: (1) sonication (15 min), (2) sonication with CO_2 sparging (15 min), and (3) three cycles of alternating sonication (5 min) and CO_2 sparging (5 min) (the total sonication and CO_2 sparging time for method 3 is equal to methods 1 and 2 (Table 2). We found, somewhat surprisingly, that aggregated latex **2d** was fairly effectively redispersed to emulsion **3d1** (D_z = 123 nm) by sonication only. However, the zeta potential of **3d1** (54 mV) was lower than that of the original colloidal solution **1d** (65 mV). This is in stark contrast to the control sample, previously described, made with CTAB and VA-044 and aggregated with NaCl, which was not effectively dispersed upon sonication. When sonication was employed in conjunction with sparging of carbon dioxide, besides the reduction of the particle size to 127 nm, the zeta potentials of **3d2** (67 mV) and **3d3** (67 mV) recovered their original value (entries 2 and 3). Particle size measurements showed monomodal distributions for **3d1**−**3d3**, with no large aggregates (Figure 4). Of the three samples, the size distribution of **3d3** was most similar to the original latex **1d**, although a small shift of the distribution to larger sizes is observed. Although the average particle sizes of the redispersed polymer colloids (~107−127 nm) were not quite as small as the original latex (84 nm), they were similar in mean size and overall particle size distribution. SEM images of the redispersed latexes **3d1**−**3d3** are shown in Figure 3. Redispersed latexes **3d1**−**3d3** were composed of individual particles or small clusters of particles. Micron-scale large aggregates were not observed. These results are the first report of redispersible polymer colloids that can be aggregated by reducing surface charge, without

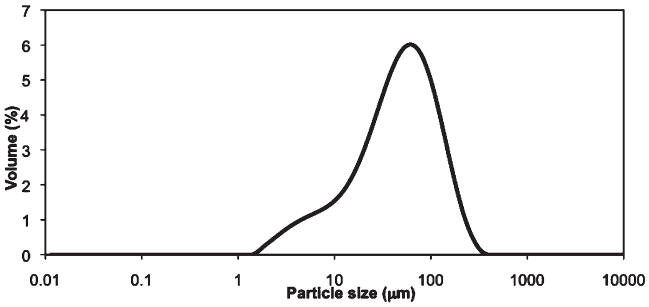


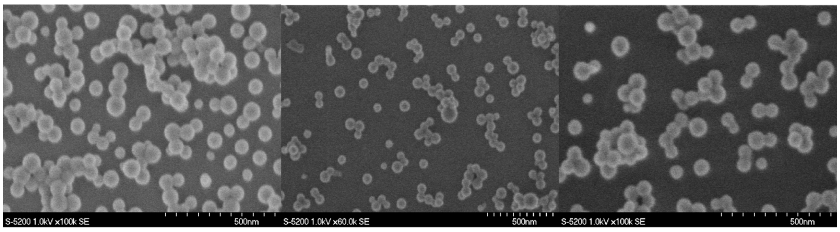
Figure 2. Particle size distributions of **2d** measured by the Mastersizer 2000.

Table 2. Redispersion of Aggregated Latex 2d to 3d by Sonication or/and Carbon Dioxide Sparging[a]

$$\mathbf{2} \xrightarrow[\substack{\text{H}_2\text{O, 20°C} \\ \text{sonication or} \\ \text{sonication + CO}_2}]{\text{redispersion}} \mathbf{3}$$

entry	treatment	3	D_z (nm)	zeta potential (mV)
1	sonication (15 min)	**3d1**	123	53
2	sonication with CO_2 (15 min)	**3d2**	127	67
3	sonication (5 min × 3) alternating with CO_2 (5 min × 3)	**3d3**	127	67

[a] Original latex **1d** had a D_z of 84 nm and a zeta potential of 65 mV.



3d1 **3d2** **3d3**

Figure 3. SEM images of redispersed latexes **3d1**−**3d3**.

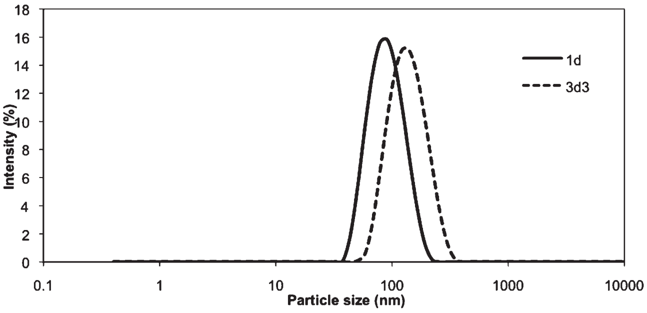


Figure 4. Particle size distributions of original latex **1d** and redispersed latex **3d3**, measured by Zetasizer ZS.

requiring addition of acid or base at each step. As noted by Fujii et al.,[5] addition of acid/base limits the number of aggregation−redispersion cycles because of salt accumulation. Our results establish the potential for truly switchable polymer colloids, capable of undergoing multiple reversible aggregation−redispersion cycles.

It is intriguing why aggregated latex **2d** redispersed comparatively well with sonication only (no CO_2 sparging) and much more effectively than the control sample. We believe that not all of the amidinium groups switched off during the aggregation step, yielding an aggregated latex with residual charge. This residual charge is not sufficient to stabilize the particles but does assist in the redispersion step. However, when only sonication is used (no CO_2 sparging), although the initial particle size can be largely recovered, the latex **3d1** is quite unstable and visibly settles in 1−2 days. In contrast, latexes sparged with CO_2 during redispersion maintain their stability for weeks if kept under CO_2 atmosphere. Further study of this phenomenon is ongoing and will be reported in a future publication.

To determine the concentration of imidazoline moieties (from the initiator) in the polystyrene, the coagulated latex **2d** was filtered, washed with water and methanol, dried, and analyzed by ^1H NMR spectroscopy. Integration of the broad peaks at 6.6 and 7.1 ppm in the ^1H NMR of entry 4 (Table 1) were calibrated to five protons to represent the aromatic protons in styrene. Integration of the imidazoline protons, 0.0206 at a shift of 3.2 ppm, was used to calculate the concentration of imidazoline moieties in the polystyrene. Analysis showed that only 0.49 mol % of imidazoline was present in the polystyrene, indicating that most of the imidazoline moieties were not bound to the chain ends. It is not clear where the remaining imidazoline groups are, but it is likely that they are in the aqueous phase of the latex. Initiator efficiencies in emulsion polymerization are typically very low (2−10%),[15] and therefore these results are not unexpected (∼5% of the imidazoline moieties were incorporated into the polystyrene). Because these groups may retain their switchability, it is possible that initiator residues in aqueous phase may affect the aggregation process by acting as an additional source of switchable moieties in the aqueous phase.

■ CONCLUSION

We have succeeded in preparing stimuli-responsive polystyrene colloids, using a simple emulsion polymerization process, that can switch between aggregated and dispersed states using nitrogen and carbon dioxide as triggers for the aggregation and redispersion steps, respectively. The switchable properties of the colloids are imparted by the use of C_{12}-amidine surfactant in combination with VA-061 bicarbonate initiator. Redispersion is most effective when both the surfactant and the initiator contain switchable amidine moieties. Nearly complete recovery of the original latex particle size distribution and zeta potential can be achieved upon redispersion. This represents the first report of redispersible polymer colloids that can be aggregated by reduction of surface charge, without requiring addition of acid or base solution at each step. Not requiring acid/base addition eliminates the problem of having a limited number of aggregation–redispersion cycles due to salt accumulation. These carbon dioxide switchable latexes establish the future potential for truly switchable polymer colloids, capable of undergoing multiple reversible aggregation–redispersion cycles.

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■ REFERENCES

(1) Guziak, L. F.; Maclay, W. N. *J. Appl. Polym. Sci.* **1963**, *7*, 2249–2258.

(2) Greene, B. W.; Nelson, A. R.; Keskey, W. H. *J. Phys. Chem.* **1980**, *84*, 1615–1620.

(3) Saija, L. M.; Uminski, M. *J. Appl. Polym. Sci.* **1999**, *71*, 1781–1787.

(4) Du Chesne, A.; Bojkova, A.; Gapinski, J.; Seip, D.; Fischery, P. *J. Colloid Interface Sci.* **2000**, *224*, 91–98.

(5) Fujii, S.; Kakigi, Y.; Suzaki, M.; Yusa, S.; Muraoka, M.; Nakamura, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3431–3433.

(6) Wang, J.; Sun, L.; Mpoukouvalas, K.; Lienkamp, K.; Lieberwirth, I.; Fassbender, B.; Bonaccurso, E.; Brunklaus, G.; Muehlebach, A.; Beierlein, T.; Tilch, R.; Butt, H.-J.; Wegner, G. *Adv. Mater.* **2009**, *21*, 1137–1141.

(7) Liu, Y.; Jessop, P. G.; Cunningham, M. F.; Eckert, C. A.; Liotta, C. L. *Science* **2006**, *313*, 958–960.

(8) Anton, P.; Laschewsky, A.; Ward, M. D. *Polym. Bull. (Berlin)* **1995**, *34*, 331–335.

(9) Sakai, H.; Imamura, H.; Kakizawa, Y.; Abe, M.; Kondo, Y.; Yoshino, N.; Harwell, J. H. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1997**, *65*, 669–672.

(10) Wongwailikhit, K.; Tasakorn, P.; Prasassarakich, P.; Aratono, M. *Sep. Sci. Technol.* **2003**, *38*, 3591–3607.

(11) Wolff, T.; Klaussner, B.; Nees, D. *J. Inf. Rec. Mater.* **1994**, *21*, 623–624.

(12) Sakai, H.; Matsumura, A.; Yokoyama, S.; Saji, T.; Abe, M. *J. Phys. Chem. B* **1999**, *103*, 10737–10740.

(13) Sakai, H.; Matsumura, A.; Saji, T.; Abe, M. *Stud. Surf. Sci. Catal.* **2001**, *132*, 505–508.

(14) Fowler, C. I.; Muchemu, C. M.; Miller, R. E.; Phan, L.; O'Neill, C.; Jessop, P. G.; Cunningham, M. F. *Macromolecules* **2011**, in press.

(15) Gilbert, R. G. *Emulsion Polymerization - a Mechanistic Approach*; Academic Press: San Diego, CA, 1995.