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Reversibly Coagulatable and Redispersible Polystyrene Latex Prepared by Emulsion Polymerization of Styrene Containing Switchable Amidine

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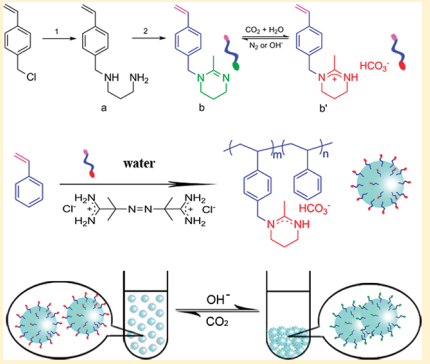
Supporting Information

ABSTRACT: An easily coagulatable/redispersible polystyrene latex system was developed in this work. The coagulatability and redispersibility of the latexes were achieved by incorporating 1.6−5.3 wt % of newly synthesized amidine-containing styrene derivative in a soap free emulsion polymerization of styrene. The resulted latex particles were coagulated by adding a small amount of caustic soda and redispersed by CO_2 bubbling, which switched amidine moieties between neutral and ionic states. The coagulation/redispersion processes were repeatable, even with washed and dried latexes. The styrene−butyl acrylate, styrene−methyl methacrylate, and styrene−acrylonitrile copolymer latexes produced with the same approach were also reversibly coagulatable and redispersible.



INTRODUCTION

Millions of tons of polymer latexes are produced annually by emulsion polymerization. The unique properties of latex products offer a variety of applications in rubber, plastic, coating, paper, textile, leather, and construction industries,[1] as well as biomedicine and pharmaceuticals.[2] Most emulsion products contain about 45−60 vol % water. Even in a high-solid content product, there is still 26−40 vol % of water present.[3] Reduction of the water content is of great interest for energy savings in polymer separation and/or in product storage and transportation.

When used in powder form, latex particles must be coagulated, filtrated, washed, and dried from latex emulsion.[4] Large amount of electrolyte or inorganic acid is often added to destabilize the latex emulsion and to coagulate the particles.[5] As these additives have a negative impact on product properties, washing is required for their removal. Substantial amount of wastewater is generated in the energy intensive coagulation/washing process. Furthermore, water washing is often not effective in removing surfactants, which are amphiphilic molecules. Less energy intensive and more environmentally benign processes for latex particle separation from emulsion are thus highly desired for sustainability of the industry.[6]

When used in liquid form such as waterborne coatings, latex particles must remain stable dispersion in water. Since production and application of emulsion products are not in the same location, about half of the transportation and storage costs are wasted in moving water from one place to another. An ideal scenario would be to coagulate latex particles on production site by an easy method, to ship the product to application site in a paste or dried form, and to redisperse the particles for uses in the required liquid form. Redispersible latex products from emulsion polymerization are indeed appealing and are of high potential to significantly contribute to the emulsion polymerization industry in meeting its sustainability challenges. Unfortunately, such easily coagulatable and redispersible latex products are not available.

Redispersibility is an important property in many latex applications, such as cement modifier, adhesive, drug encapsulation, and polymer electronics, which require latex products in a redispersible powder form.[7] The current practice is to add an adequate amount of protective stabilizer. For example, poly(vinyl alcohol) or poly(acrylamide) are added to poly(vinyl acetate) or polyacrylate for redispersion in water.[7b] However, thus produced latexes have substantially different properties from their original ones in terms of particle sizes and chemical contents. Redispersion of polymer particles can also be achieved by introducing functional groups such as carboxylated[7a,c] and sulfonated[7d] onto particle surfaces or to the shell portion of core−shell particles.[7a,d] However, the redispersion of carboxylated particles is highly pH-

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dependent. Furthermore, these powders are produced from spray-drying, freeze-drying, or rotating flash-drying processes.[7] Additional water is used to dilute latex to prevent nozzle plugging in spray-drying concentrated products. These processes acquire high costs in energy consumption and operation.

Latex coagulation and redispersion are greatly influenced by the type and amount of surfactants used. Conventional surfactants are physically adsorbed onto particle surfaces and stabilize the particles in emulsion polymerization and storage. It is challenging to destabilize such latex particles, which is normally done by adding large amount of salts or acids. After coagulation, the surfactant molecules lose their abilities of stabilization and the coagulated particles cannot be redispersed into water to form a stable latex product. Over the years, several types of switchable surfactants have been reported. These surfactant molecules bear functional groups that can be switched alternatively between surface-active or surface-inactive forms by some triggers.[8−12] However, none has been applied in preparation of polymer latexes. Intuitively, such a surfactant can be activated and used as stabilizer in emulsion polymerization, and be deactivated after polymerization for latex coagulation. Whenever needed, it can be reactivated again to facilitate redispersion of the latex particles. Reversible coagulation and dispersion can thus be achieved by "switching" the surfactant.

Recently, Jessop et al.[13] reported the use of long-chain alkyl amidine compounds as switchable surfactant for controlling stability of alkane in water emulsion. Surface activities of the surfactants were turned on and off by bubbling CO_2 and N_2 (or Ar) gases. CO_2 in water reacts with amidine to form bicarbonate salt that stabilizes emulsion. Bicarbonate salt decomposes to amidine to break the emulsion in the presence of N_2 or Ar.[14] Microsuspension polymerization of styrene (St) was carried out with *N*′-dodecyl-*N*,*N*-dimethylacetamidinium bicarbonate as the surfactant under CO_2 at 65 °C.[13] The amidine surfactant effectively stabilized the microsuspension during polymerization. It was deactivated by bubbling Ar or N_2 after polymerization and coagulation occurred as anticipated. Unfortunately, there was no report if the coagulated particles could not be reversibly redispersed and coagulated by bubbling CO_2 and N_2.

Since desorption of physically absorbed surfactant molecules from particle surfaces occurred during the coagulation process,[15] we hypothesize that a reversibly coagulatable and redispersible latex product is achievable if amidine moieties can be covalently bounded to the particle surfaces. Our approach is to incorporate small amount of amidine-functionalized comonomer in the emulsion polymerization of St. Reported in this paper are synthesis of a switchable amidine monomer, 2-methyl-1-(4-vinylbenzyl)-1,4,5,6-tetrahydropyrimidine (**b**), soap-free emulsion polymerization of St or St/butyl acrylate, St/methyl methacrylate, or St/acrylonitrile with the amidinium bicarbonate **b**′, and demonstration of reversible coagulation and dispersion of the PS latex products. The trigger we use for coagulation is a small amount of caustic soda and that for redispersion is CO_2 bubbling.

EXPERIMENTAL SECTION

Materials. 1,3-Diaminopropane, 4-chloromethylstyrene, and *N*,*N*-dimethylacetamide dimethyl acetal (98%) were purchased from Acros and were used without further purification. Dichloromethane, chloroform, acetonitrile, DMSO, ethanol, ether, and tetrahydrofuran (THF) were supplied by Sinopharm Chemical Reagent Co. Other chemicals were analytical-grade reagents and were used as received. All aqueous solutions were prepared with deionized (DI) water. Carbon dioxide (dry ice grade) and nitrogen (99.999%) were purchased from Jingong Air Co. Styrene (St), butyl acrylate (BA), methyl methyacylate (MMA), and acrylonitrile (AN) were all distilled under vacuum prior to use. Dodecylamine hydrochloride was prepared by reaction of dodecylamine with HCl in ethanol and recrystallized in ether. The initiator, 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50), was supplied by Qingdao Runxing Photoelectric Material Co.

Synthesis of *N*-(4-vinylbenzyl)propane-1,3-diamine (a)[16]. A solution of 4-chloromethylstyrene (17.1 mL, 0.12 mol) in dichloromethane (100 mL) was dropped slowly to a solution of 1,3-diaminopropane (50 mL, 0.60 mol) in dichloromethane (500 mL) at 0 °C. The reaction was maintained at 0 °C for 24 h. The mixture was washed with 250 mL of DI water twice. The organic layer was collected and was dried over anhydrous Na_2SO_4. After the removal of Na_2SO_4, the solvent was evaporated to obtain **a** (20.4 g, 0.107 mol, 89.3%) as an orange syrup.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.26−7.38 (dd, 4H, Ar H), 6.67−6.74 (q, J = 10.9 Hz, 1H; CH), 5.71 (d, J = 17.5 Hz, 1H; CH_2═), 5.21 (d, J = 11.0 Hz, 1H; CH_2═), 3.79 (s, 2H; Ar−CH_2), 2.79 (t, J = 6.7 Hz, 2H; $NHCH_2$), 2.71 (t, J = 6.8 Hz, 2H; CH_2NH_2), 1.66 (m, J = 6.8, 6.9 Hz, 2H; CCH_2C), 1.50 (s, 3H; NH, NH_2).

Synthesis of 2-Methyl-1-(4-vinylbenzyl)-1,4,5,6-tetrahydropyrimidinium Bicarbonate (b′). *N*,*N*-Dimethylacetamide dimethyl acetal (35 mmol, 4.66 g) and hydroquinone (0.3 mmol, 33 mg) were added into a solution of a (30 mmol, 5.71 g) in chloroform (50 mL). The mixture was heated to 65 °C for 1 h. The solvent was evaporated. Wet acetonitrile was then added. After bubbling the mixture with carbon dioxide for 0.5 h, a white precipitate was obtained. The mixture was kept at −24 °C overnight. The precipitate was collected by filtration. The filtrate was then concentrated under reduced pressure. The aliquot was bubbled with carbon dioxide again for another 0.5 h to obtain a second batch of precipitate. The product was dried under vacuum with an overall yield of 4.32 g of **b**′ (15.6 mmol, 52.1%). The purity of **b**′ was over 99%.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.11−7.39 (dd, 4H, Ar H), 6.64−6.71 (q, J = 10.9 Hz, 1H; CH), 5.73 (d, J = 17.6 Hz, 1H; CH_2═), 5.23 (d, J = 10.8 Hz, 1H; CH_2═), 4.45 (s, 2H; Ar−CH_2), 3.39 (t, J = 4.9 Hz, 2H; ═NCH_2), 3.21 (t, J = 5.4 Hz, 2H; NCH_2), 2.19 (s, 3H; CH_3), 1.88 (t, J = 5.5 Hz, 2H; CCH_2C). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 161.0 (HCO_3^-), 157.6 (C═N), 137.1 (CH), 136.0 (═CH−C), 135.8 (CH_2−C(Ar)), 126.7−126.6 (4C Ar), 114.2 (═CH_2), 54.3 (Ar−CH_2), 46.1 (═NCH_2), 42.0 (NCH_2), 20.8 (CH_3), 20.4 (CH_2-CH_2CH_2). MS (ESI, m/z): $[M + H]^+$ calcd for $C_{14}H_{19}N_2$, 215.15; found, 215.1.

Synthesis of Polystyrene Latexes by Emulsion Polymerization of Styrene with b′. St (4.55 g) and comonomer **b**′ (0.075−0.25 g) were added to a 50 mL of three-necked flask containing 19 g of DI water. The mixture was agitated at 500 rpm and was purged with nitrogen for 15 min and then carbon dioxide for 30 min. The required amount of initiator V-50 was dissolved in 1 g of water and was added to the emulsion system by a syringe. The mixture was quickly heated to 70 °C at 300 rpm. The polymerization was conducted for 8 h. The monomer conversion was determined gravimetrically. The freeze-dried latex samples were prepared for GPC and NMR measurements.

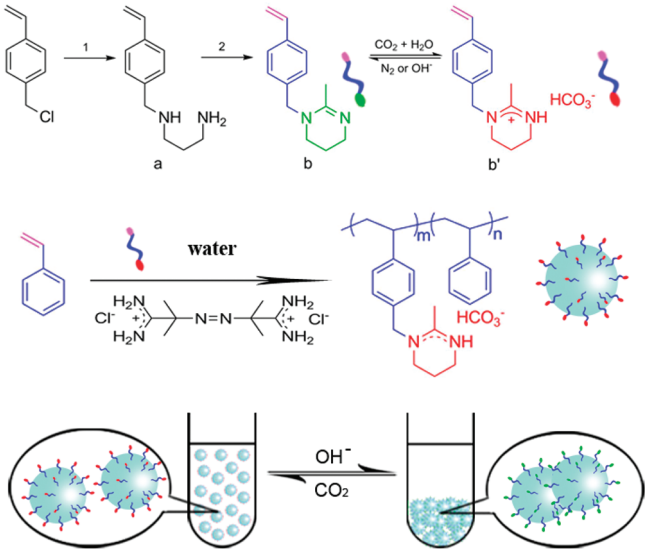
Synthesis of Styrenic Copolymer Latexes by Emulsion Copolymerization Using b′. St/BA or St/MMA or St/AN (4.55 g), **b**′ (0.125 g), and dodecylamine hydrochloride (only in run E-S5 as surfactant) were added to a 50 mL three-necked flask containing 19 g of DI water. The mixture was agitated at 500 rpm and was purged with nitrogen for 15 min and then carbon dioxide for 30 min. The required amount of initiator V-50 was dissolved in 1 g of water and was added to the emulsion system by a syringe. The mixture was quickly heated to 70 °C at 300 rpm. The polymerization was conducted for 8 h. The monomer conversion was determined gravimetrically. The freeze-dried

Table 1. Recipes for Emulsion Polymerizations/ Copolymerizations of St Using b′

run	E1-E8	E-S1 - E-S5[a]
monomer [g]	4.55	4.55
DI water [g]	20	20
b′ [g]	0.075 - 0.25	0.125
V-50 [mg]	47 - 94	47

[a] 0.125 g of dodecylamine hydrochloride was added as surfmer in Run E-S5.

Scheme 1. Synthesis Routes of Switchable Amidine Comonomer and Its Emulsion Polymerization with Styrene, as well as a Sketch of Reversible Coagulation and Re-Dispersion of Polystyrene Latex Triggered by Carbon Dioxide and a Small Amount of Caustic Soda



latex samples were prepared for GPC and NMR measurements. The recipes for emulsion polymerization are tabulated in Table 1.

Coagulation and Redispersion of Latexes. 0.1 M NaOH solution (0.1−0.5 mL per gram latex) was added to the latex at room temperature to adjust the pH value to 9−10 to conduct the coagulation. In redispersing the coagulated PS particles into the same solution or a fresh DI water, the mixture was bubbled with CO_2 for several minutes, followed by ultrasound. The bubbling and ultrasound processes were repeated for three or four times until stable latex was obtained. The coagulated particles were separated from solution by centrifugation and were washed with fresh DI water three times until the paste had pH value about 8. The paste was dried at room temperature under vacuum to yield a powder product.

Characterizations. ^1H and ^{13}C NMR spectra were acquired in a Bruker Advance 2B 400 MHz spectrometer. ESI/MS measurement was conducted using a Finnigan LCQ DECA XPplus instrument (150−2000 m/z). The conductivity of **b′** in DMSO was measured using a Lei-ci conductivity meter DDSJ-308A at 25 ± 0.2 °C. Prior to the conductivity measurement, the solution was bubbled with N_2 for 1 h until a stable conductivity was reached. The particle size and distribution were determined by a Malvern Zetasizer 3000HSA (670 nm, 3 mW, 90° scattering angle) at 25 °C. The molecular weight was measured using a Waters GPC comprising a Waters 1525 HPLC Pump, a Waters 2414 Refractive Index Detector, and a Waters 717 Autosampler. The eluent was THF at a flow rate of 1.0 mL/min and the temperature was 35 °C. A set of three Waters Styragel Columns (HR 5, 4, 3) were used. The molecular weight and PDI were derived from a calibration curve based on narrow polystyrene standards. The morphology of particles was visualized using a JEM-1200EX TEM.

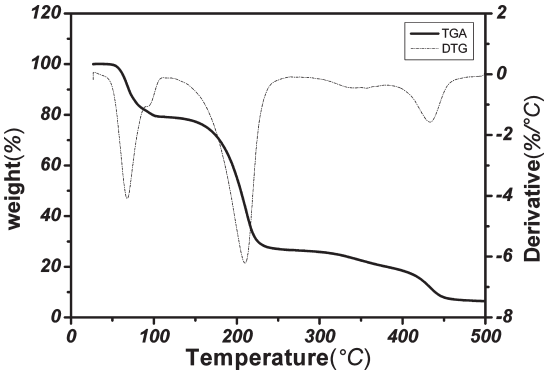


Figure 1. TGA and DTG curves of b′.

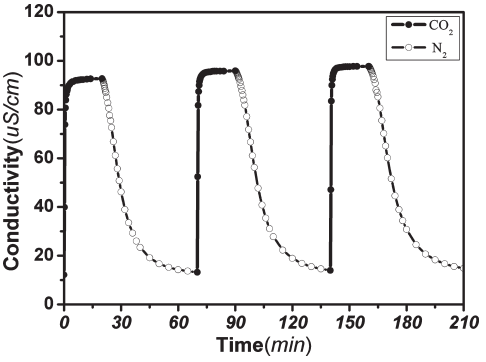


Figure 2. Variations of the conductivity of b′ in DMSO solution (10 mM) at 25 °C versus time during three cycles of alternating purging with CO_2 and N_2.

RESULTS AND DISCUSSION

Characterization of Amidine Monomer b′. The synthesis of the amidine monomer, 2-methyl-1-(4-vinylbenzyl)-1,4,5,6-tetrahydropyrimidine (**b**), and its bicarbonate **b′** is shown in Scheme 1.

To investigate the thermal stability of the bicarbonate salt, **b′** saturated with CO_2 was determined by a thermogravimetric analysis (TGA), with its spectrum shown in Figure 1. There existed three platforms with the maximum decomposition occurred at 210.1 °C. The material started to decompose at 58.7 °C, and the rate in the first platform reached a maximum value at 67.7 °C. The mass loss in the first platform was 22.4%, which fully agreed with the theoretical mass of CO_2 and water associated with **b′**. The formation of bicarbonate salt was further confirmed. In our experiments, the amidinium bicarbonate salt **b′** was stored under a dry CO_2 atmosphere and low temperature to avoid decomposition.

The conductivity of 10 mM of **b′** in dimethyl sulfoxide (DMSO) was determined at 25 ± 0.2 °C for three cycles of alternatively CO_2 or N_2 bubbling. The result is shown in Figure 2. The conductivity of the solution increased from 12.1 to 92.7 μS/cm in 20 min and leveled off when CO_2 was bubbled. It reduced to its initial value in 50 min upon bubbling with N_2.

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Table 2. Experimental Conditions and Polymer and Particle Results from the Emulsion Polymerization of Styrene with Switchable Amidine Comonomer b′[a]

run	[b′]/[St] × 10^2	[I]/[St] × 10^{3b}	x [%][c]	F_b × 10^{2d}	M_w [kD][e]	M_w/M_n[e]	N_p [10^{17}/L][e]	D_z [nm][f]	D_v/D_n[f]
E1	0.6	4	94.5	0.8	106	12.8	1.94	122.4	1.07
E2	0.6	8	96.4	0.7	103	13.8	1.01	153.3	1.11
E3	1.0	4	92.8	1.1	99	14.6	2.85	105.8	1.10
E4	1.0	8	94.3	1.2	85	11.5	1.70	128.7	1.09
E5	1.6	4	92.8	1.5	78	11.7	4.11	96.7	1.06
E6	1.6	8	94.1	1.7	74	11.3	1.43	141.5	1.02
E7	2.1	4	91.0	2.3	197	13.2	0.80	167.0	1.12
E8	2.1	8	94.7	2.2	109	13.4	0.94	161.5	1.18

[a] All runs contained 4.55 g of St and 20 g of water, and were carried out at 70 °C and 300 rpm for 8 h. [b] Initiator is V-50. [c] x is the overall monomer conversion. [d] The molar ratio of switchable amidine monomer **b** in the copolymer as measured by ^{1}H NMR. [e] M_w is the weight-average molecular weight of PS measured by Waters GPC. [f] D_z, D_v, and D_n are the respective z-, volume-, and number-average particle diameters determined by Malvern Particle Sizer; N_p is the number of PS particles per liter of the latex.

The successive cycles gave similar conductivity data, which showed good reversibility and repeatability of the amidine. A small increase of 2−3 μS/cm was observed in each cycle due to evaporation of the solvent. Good switchability of **b** by CO_2 and N_2 bubbling is clearly demonstrated.

Synthesis of Polystyrene Latexes by Emulsion Polymerization of Styrene with b′. The amidinium bicarbonate **b′** was employed as comonomer in soap-free emulsion polymerization of St (Scheme 1). 0.6−2.1 mol % (equivalent to 1.6−5.3 wt %) of **b′** was used to introduce cationic groups to particle surfaces to stabilize the emulsion. The copolymerization was initiated by 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50) and was carried out under CO_2 atmosphere at 70 °C for 8 h. The experimental conditions, as well as monomer conversion, polymer molecular weight, and particle size data are summarized in Table 2. All runs yielded stable PS latexes. The samples were stored at room temperature for more than 7 months without any separation. The overall monomer conversions were between 91.0 and 96.4%. Limited monomer conversions were often observed in soap-free emulsion polymerization systems,[17] and were attributed to diffusion-controlled propagation reactions at high conversions.[18] The ^{1}H NMR measurements (shown in the Supporting Information) of the resulted copolymer samples after freeze-drying, in which the unreacted St and water contents were removed but the unreacted **b′** should remain if any, showed that the molar fractions of **b′** (F_b) agreed with their comonomer ratios. There were no residual vinyl groups determined at the chemical shifts of 5.2 and 5.7 ppm, suggesting complete incorporation of **b′** into the copolymers.

The polymer particles had Z-average diameters (D_z) between 96.7 and 167.0 nm and were nearly monodispersed with the size distributions D_v/D_n around 1.02−1.18. There were (0.8−4.1) × 10^{17} PS particles per liter of latex. The weight-average molecular weights (M_w) were in the range of (0.7−2.0) × 10^5, with M_w/M_n between 8.8 and 13.4. The high polymer polydispersities were common in soap-free emulsion polymerization systems.[19]

Four levels of **b′** concentration and two levels of initiator concentration were employed in the emulsion polymerization experiments. The particle size appeared decreased first and increased later with the **b′** concentration (i.e., the number of particles N_p increased first and decreased later). The first decrease in the size was due to the high monomer concentration in water phase for homogeneous nucleation, while the later increase was probably caused by bridging flocculation of the growing particles at the presence of a high level of polyelectrolyte as observed in other monomer systems in soap-free emulsion polymerization.[20] A similar trend was also found in the variation of polymer molecular weight versus the **b′** concentration.

Reversible Coagulation and Redispersion of Latexes. The styrene derivative synthesized in this work could be readily switched between **b** and **b′** by CO_2 and N_2 purging. The switchability of the produced PS latexes was also examined with N_2 and CO_2. However, it was observed there was no coagulation occurred when the latex emulsion was bubbled with N_2 even at an elevated temperature of 80 °C. To our disappointment, N_2 was unable to switch the amidinium bicarbonate back to the neutral amidine at the particle surfaces. Fortunately, we found that the latex particles were readily coagulated and precipitated out by adjusting pH value of the latex emulsion from 7 to 9−10 with 0.1 M of caustic soda.

The soda concentrations required to trigger the coagulation were low at 10−50 mM NaOH, i.e., 0.1−0.5 mL of 0.1 M NaOH solution per gram of latex emulsion. In comparison, the critical coagulation concentrations (CCC) of electrolytes were reported to be in the range of 360−930 mM of KBr for sulfonated PS latexes,[21a] 750−1142 mM of NaCl for polyacrylic latexes,[21b] and 320−440 mM of KCl for PS latexes,[21c] respectively. The actual electrolyte concentrations used in practice were much higher than these CCC's to fully destabilizing latexes. The soda concentrations in this work were only in a small percentage of the salts used in the practices.

The PS latex particles were clearly separated from water after coagulation with soda. Figure 3 shows a typical example of run E2 latex sample. The samples obtained from other runs had the same performance in coagulation. Adding excessive water or applying centrifugation operation accelerated the particles settling. The coagulated particles were redispersed to the same solution by bubbling CO_2 followed by ultrasound for three to four times. All the coagulated PS particles were well dispersed and restabilized. There was no precipitate observed during the coagulation-redispersion cycle. Stable latex emulsions with slightly bluish appearance after redispersion were obtained as shown in Figure 3. The pH values of the emulsions were the same as their original values of approximately 7.

The coagulation and redispersion processes were repeated by three cycles for run E2 sample. All the cycles had the same observation as the first one. To examine the stability of amidine groups on particle surface, the coagulated particles were

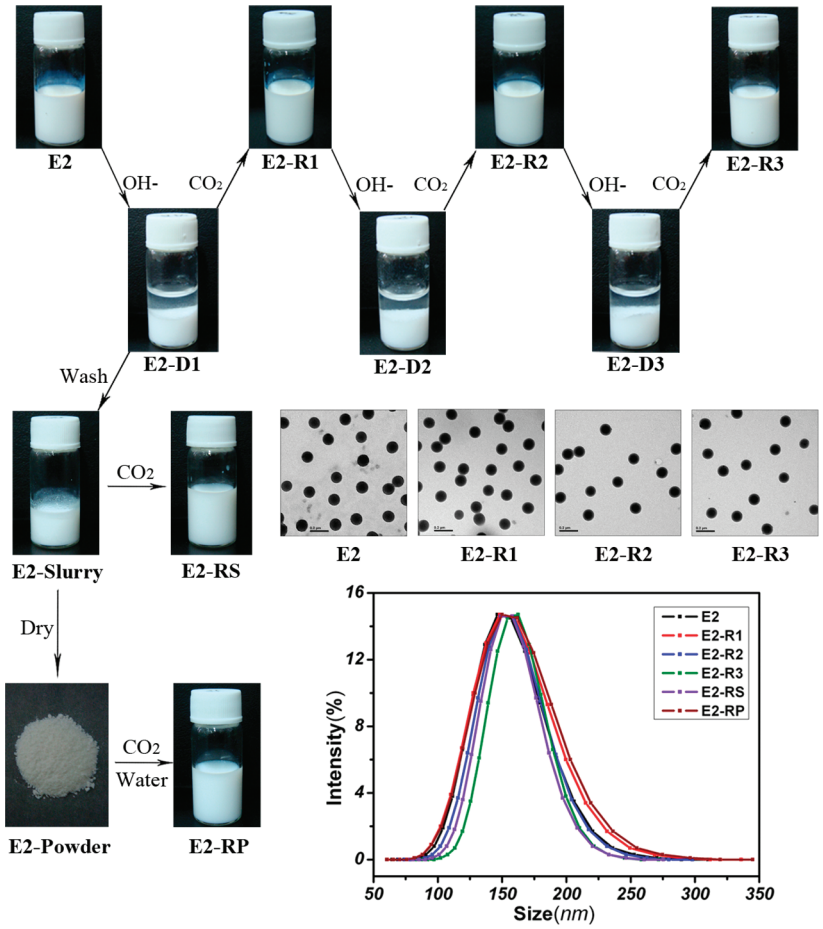

Figure 3. Three cycles of latex coagulation (E2-D1∼E2-D3) with samll amount of caustic soda and redispersion (E2-R1 to E2-R3) of the coagulated particles with CO_2 bubbling for Run E2 sample, as well as the redispersion of the washed (E2-RS) and dried (E2-RP) particles.

separated from solution and were washed with fresh DI water three times. The paste of the coagulated particles after washing was still readily dispersible into fresh water to form a stable latex emulsion using the same procedure. Moreover, the paste was dried at room temperature under vacuum to obtain a powder product. It was jubilant to find that the powder was also readily dispersed into fresh water using the same procedure to form a very stable latex emulsion. The results were very reproducible.

Figure 3 shows the photos of the run E2 samples in the three cycles of coagulation and redispersion processes, as well as in the redispersion of the slurry and powder products. Their particle size distributions were determined by a Malvern Particle Sizer. The average particle sizes after each process changed very slightly with a maximum of 6 nm increase compared to its original size. The size distribution remained almost the same, as also evident from the included TEM images. Most of particles were nicely isolated from each other with little aggregation. An examination of a few aggregated particles also revealed that there were clear interfaces between particles, suggesting a very weak adhesion. All the latex samples prepared from the emulsion polymerization runs in this work were thoroughly investigated for their coagulatability and redispersibility and all the measurements gave consistently good results as run E2.

Figure 4 summarized the data of the average particle diameter (D_z) and the number of particles per liter of latex emulsion (N_p). The N_p was calculated from the particle size distribution of the

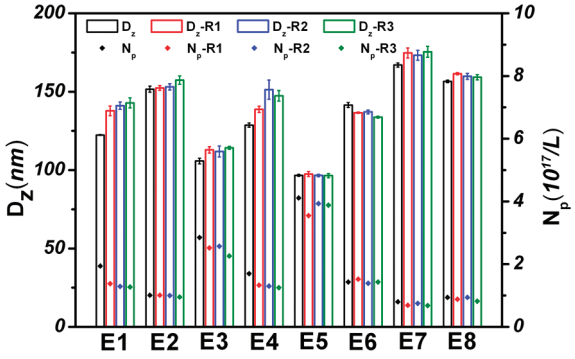

Figure 4. Variation of the Z-average diameter and that of the number of particles per liter of latex for all the polystyrene latex samples and their redispersed forms with three cycles of coagulation and redispersion. For each run from left to right: original (black), R1 (red), R2 (blue), and R3 (green).

latex. All the runs had the N_p values between 0.7×10^{17} and 4.1×10^{17} particles per liter of latex. In the three-cycle coagulation/redispersion processes, the D_z values increased by an average of 5% after three cycles, with the largest increase of 16% (E1-R3). Correspondingly, the decreases in N_p were approximately 12% after three cycles with the maximum 34% in run E1-R3. These increases in D_z or decreases in N_p were caused by aggregation of a small fraction of the particles.

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Table 3. Experimental Conditions and Polymer and Particle Results of the Emulsion Copolymerization[a]

run	monomer system [wt %]	x_1 [%][b]	$F_b \times 10^2$[c]	M_w [kD][d]	M_w/M_n[e]	D_z [nm][e]	D_z-R1 [nm][e]	D_z-R2 [nm][e]	D_z-R3 [nm][e]
E-S1	St:BA = 50:50	95.9	1.1	83	6.4	111.2	126.5	161.2	176.0
E-S2	St:BA = 70:30	96.2	1.1	82	6.6	107.9	132.1	131.4	132.3
E-S3[f]	St:MMA = 70:30	~100	1.0	109	13.3	128.7	129.4	130.1	131.5
E-S4	St:AN = 77:23	93.8	0.8	136	10.4	267.6	281.9	277.9	273.6
E-S5[g]	St	99.9	1.0	82	11.3	77.2	87.6	84.2	93.8

[a] All runs contained 4.55 g of monomer system, 47 mg of V-50, 0.125 g of **b′** and 20 g of water, and were carried out at 70 °C and 300 rpm for 8 h. [b] x_1 is the overall conversion of monomer system, determined gravimetrically. [c] The molar ratio of switchable amidine monomer **b′** in the copolymer as measured by ^{1}H NMR. [d] M_w and M_n are the weight- and number-average molecular weight of PS measured by Waters GPC, respectively. [e] D_z, D_z-R1, D_z-R2, and D_z-R3 are respectively the *z*-average particle diameters of the original latex, redispersed latex from cycle 1, cycle 2, and cycle 3, determined by Malvern Particle Sizer. [f] The z-average particle diameters of slurry and dry powder obtained after cycle 1 coagulation were 128.1 and 130.1 nm respectively, determined by Malvern Particle Sizer. [g] 0.125 g dodecylamine hydrochloride was added as surfactant.

Synthesis of Styrenic Copolymer Latexes by Emulsion Copolymerization with b′. To demonstrate versatility of the developed method, we examined several industrially important styrene-acrylate copolymer latexes. The copolymerization runs of St with butyl acrylate (BA) at the weight ratios of 50:50 (run E-S1) and 70:30 (run E-S2), and methyl methacrylate (MMA) at 70:30 (run E-S3) in the presence of **b′** were carried out. The experimental conditions and polymer and particle results are shown in Table 3. The latexes of runs E-S1 to E-S3 were reversibly coagulatable and redispersible. A substantial increase of particle size in run E-S1 after three-cycles of coagulation/redispersion was mainly attributed to the low T_g of the copolymer, resulting in some particle aggregation. The paste of the coagulated St/MMA copolymer particles (run E-S3) after washing with DI water was readily redispersed into fresh water to form a stable latex emulsion. The powder obtained after drying the paste at room temperature under vacuum was still redispersible in fresh water. We also examined the copolymerization of St/AN of 77:23 (run E-S4) in the presence of **b′** and observed good redispersibility of the latex. Furthermore, conventional emulsion polymerization of St with added dodecylamine hydrochloride as surfactant in the presence of **b′** was carried out (run E-S5). The resulted latex was also reversibly coagulatable and redispersible.

CONCLUSIONS

In summary, we have successfully developed a coagulatable and redispersible polystyrene latex system. The latexes were prepared through a soap-free emulsion polymerization of styrene or styrene/butyl acrylate, styrene/methyl methacrylate, or styrene/acrylnitrile with a styrene derivative bearing amidine group. The amidine-containing comonomer was reversibly switchable between ionic and neutral states by alternatively bubbling CO_2 and N_2. Such a comonomer incorporated into the polystyrene chains acted as an effective stabilizer during the emulsion polymerization. The latex particles thus formed could be easily coagulated by adding small amount of caustic soda. The coagulated particles could be redispersed into water to prepare a stable latex without adding extra stabilizer. The coagulation and redispersion processes were repeatable. It was particularly plausible that the aggregated particles after washing and drying were still redispersible. Such coagulatable/redispersible latex system prepared directly from an emulsion polymerization is believed to have high potential in cost savings in the areas of separation, storage, and transportation and thus to benefit our economy and environment.

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra of polymer, stability of **b′** and amidine group in polymer, and GPC trace of polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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