ACS Macro Letters

Letter

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2-(Diethyl)aminoethyl Methacrylate as a CO_2-Switchable Comonomer for the Preparation of Readily Coagulated and Redispersed Polymer Latexes

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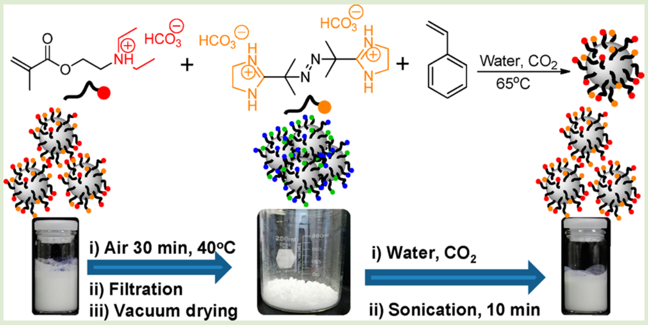
Supporting Information



ABSTRACT: CO_2 stimuli-responsive polystyrene latexes having a solids content of 27% were prepared in a surfactant-free emulsion polymerization (SFEP) under a CO_2 atmosphere, employing only commercially available chemical compounds: styrene, the initiator VA-061, and 0.54 mol % of the CO_2-switchable comonomer DEAEMA. The resulting polymer particles are 230−300 nm in diameter and are monodisperse (PDI ≤ 0.054), as confirmed by DLS, TEM, and SEM. Although they are stable under a CO_2 atmosphere, the latexes can be easily destabilized by the bubbling of air through the sample at 40 °C, allowing for recovery of the particles by filtration. Recovered polymer particles can be dried to powder and readily redispersed in carbonated water, yielding latexes with very similar zeta-potential and particle size as the original latexes. In addition, the bicarbonate salt of poly(DEAEMA) formed during the polymerization has been found to act as a CO_2-switchable flocculant, thus, facilitating the coagulation of the latex without altering the properties of the latex after redispersion.

The development of easily coagulable/redispersible polymer latexes is of significant interest from both scientific and industrial perspectives.[1−10] Facile coagulation of latexes would allow the recovery of polymer particles from the latex to be used in a powder form when needed. Furthermore, there would be savings in energy and transportation costs if the polymer powders (stored and delivered as a dry powder) could then be redispersed in water for final latex use. Many polymer latexes are also coagulated to be used as resins. Coagulation of latexes is usually achieved by addition of chemicals to the latex (e.g., salt, acid, or base) which can be undesirable in the final product.[11,12] Additional processing steps are then required to remove them, resulting in an additional waste stream. The ability to rapidly and easily alter the polymer dispersion from a suspended to an aggregated state without using salt or acid could provide significant environmental and economic benefits.[1−6,8−10,13] Furthermore, the continued presence of surfactants in the polymer dispersion can in some cases negatively affect the final performance of the material. Thus, a surfactant-free emulsion polymerization (SFEP) that can be reversibly coagulated and redispersed using only CO_2 as an external trigger appears to be the best way to avoid the drawbacks of both coagulation by chemicals and the presence of surfactant.[6,10]

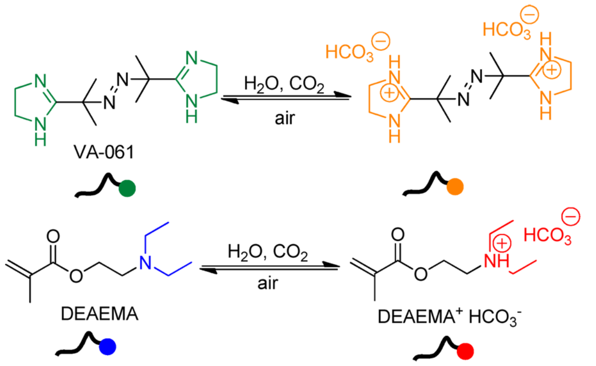
Recent studies, employing amidine-functionalized comonomers, were reported by Zhang et al.[8,10] However, due to the presence of amidinium hydrochloride salts at the surface of the particles, arising from the decomposition of the 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50) initiator, addition of NaOH was necessary to trigger destabilization of the latex.[8] In addition, synthesis of the amidine-containing comonomers required several steps and the use of volatile organic solvents.[8,10] The use of only commercially available materials in such a process would add several benefits for the commercialization of the resulting products. Our group recently described the synthesis of a CO_2-triggered switchable latex in a surfactant-free emulsion polymerization using only the commercially available initiator 2,2′-azobis[2-(2-imidazolin-2-yl)propane] (VA-061) as particle stabilizer.[6] However, it allowed the formation of latexes containing no more than 7% solids content, showing that further research was required before these could be considered industrially relevant materials.

In the course of our studies of switchable solvents and surfactants, it was found that hydrophobic tertiary amines can reversibly react with CO_2 to become soluble in water.[1,14,15] Monomers bearing such functional groups can react in the same manner. This has been recently demonstrated by Zhao et al.,[16] who took advantage of the switchability of 2-(dimethylamino)ethyl methacrylate (DMAEMA) to prepare different CO_2 stimuli-responsive block and random copolymers. On their side and in a similar manner, Zhang et al. also reported the synthesis of poly(DMAEMA)-based block

Received: June 22, 2012
Accepted: July 30, 2012
Published: August 20, 2012

copolymers by RAFT polymerization, which were further employed as a polymeric surfactant.[9] Such monomers, when copolymerized with hydrophobic monomers, may also be used as stabilizers for emulsion polymerizations under CO$_2$ atmosphere. We investigated 2-(diethyl)aminoethyl methacrylate (DEAEMA) as a switchable comonomer (Scheme 1) for the SFEP of styrene (St) initiated by the switchable azo-initiator VA-061 (Scheme 1) in order to prepare CO$_2$-responsive latexes (Scheme 2). For this work, we prefer DEAEMA over DMAEMA because, once polymerized, the latter shows a LCST around 40 °C (in a CO$_2$-free environment)[16] and hence would be water-soluble in both charged and uncharged states, thereby preventing coagulation of the latex at room temperature.

Scheme 1. Switchable Behavior of DEAEMA and VA-061 in the Presence/Absence of CO$_2$



Scheme 2. Preparation of a Switchable Polymer Latex and Reversible Aggregation and Redispersion of the Latex Triggered by Removal and Addition of CO$_2$

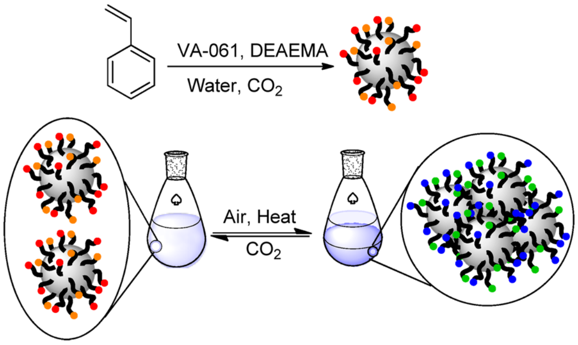


Table 2. Reversible Aggregation/Redispersion of the Latexes

entry[a]	original Z-diameter in nm (PDI)[b]	Z-diameter after destabilization in μm[c]	Z-diameter after restabilization in nm (PDI)[b]	ζ-potential after restabilization[d] (mV)
3	300 (0.02)	8.4	563 (0.48)[f]	9.4
4	230 (0.04)	5.7; 13.5[e]	286 (0.06)[g]	41.3
5	279 (0.03)	0.2; 38.2[e]	330 (0.09)[g]	35.2
6	280 (0.04)	0.2; 158.4[e]	407 (0.44)[g]	49.3

[a]Entry numbers correspond to entries in Table 1. [b]Values of PDI obtained from Zetasizer ZS that are <0.1 indicate a narrow, monomodal size distribution. [c]Determined using a Malvern Mastersizer 2000 (graphs of volume average diameter are shown in Figure S3). [d]Measured using a dip cell. [e]Values obtained after destabilization in the presence of poly(DEAEMA). [f]Not sonicated. [g]Restabilization performed after destabilization in the presence of poly(DEAEMA).

The order of addition of the reagents strongly affects the results. A first experiment (entry 1, Table 1), targeting a latex of 27% solids content, was performed by bubbling CO$_2$ through a mixture of water, styrene, and DEAEMA, followed by the addition of a carbonated solution of the initiator. Using only 0.06% of VA-061 and 0.54% of DEAEMA (with respect to monomer), a stable latex having a particle size of 134 nm with a PDI of 0.02 was obtained. However, no more than 12% monomer conversion was reached. When the same experiment was performed by a slight modification of the procedure (entry 2, Table 1), consisting of "switching on" DEAEMA separately and adding it to the styrene/water mixture, an increase in monomer conversion from 12 to 41% was observed. From these two experiments it can be assumed that, in a hydrophobic environment (here referred to as the styrenic phase), formation of DEAEMA$^+$HCO$_3^-$ is more difficult due to the low amount of water locally present. When DEAEMA is fully converted to DEAEMA$^+$HCO$_3^-$ before its addition to the reaction media, in situ formation of surfactant is favored, leading to more efficient nucleation, a higher number of particles, and thus, to a faster rate of polymerization.

Nevertheless, the relatively low conversion observed in entry 2 lets us conclude that most of the initiator was likely consumed in the formation of a water-soluble polymer, as reported for other surfactant-free emulsion polymerizations performed in the presence of water-soluble monomers.[17] Another argument in favor of water-soluble polymer formation is the greater concentration of DEAEMA$^+$ HCO$_3^-$ (0.245%$_{mol}$ assuming complete solubility of the introduced comonomer) than styrene (water solubility of 0.041%$_{mol}$ at 60 °C[18]) in the aqueous phase.

Table 1. Surfactant-Free Emulsion Polymerization of Styrene in the Presence of DEAEMA[a]

entry	[MMA]/[St] (%$_{wt}$)	[VA-061]/[St+MMA] (%$_{mol}$)	[DEAEMA]/ [St+MMA] (%$_{mol}$)	conversion (%)	particle size, nm (PDI)[b]	ζ-potential (mV)[c]	N_p[d] (10^{16}/L)
1[e]		0.06	0.54	12	134 (0.02)		2.0
2		0.06	0.54	41	229 (0.04)	48	1.2
3	5.1	0.06	0.54	71	300 (0.02)	50	1.0
4	5.1	0.15	0.54	74	230 (0.04)	32	2.3
5	5.1	0.25	0.54	90	279 (0.03)	42	1.5
6	5.1	0.15	0	64	280 (0.04)	40	1.0

[a]Reactions were carried out for 15 h at 65 °C under CO$_2$ bubbling, targeting 27% solid content. [b]Values of PDI obtained from Zetasizer ZS that are <0.1 indicate a narrow, monomodal size distribution. [c]Measured using a dip cell. [d]N_p is the number of PS particles per liter of latex. [e]DEAEMA mixed with styrene and water before sparging.

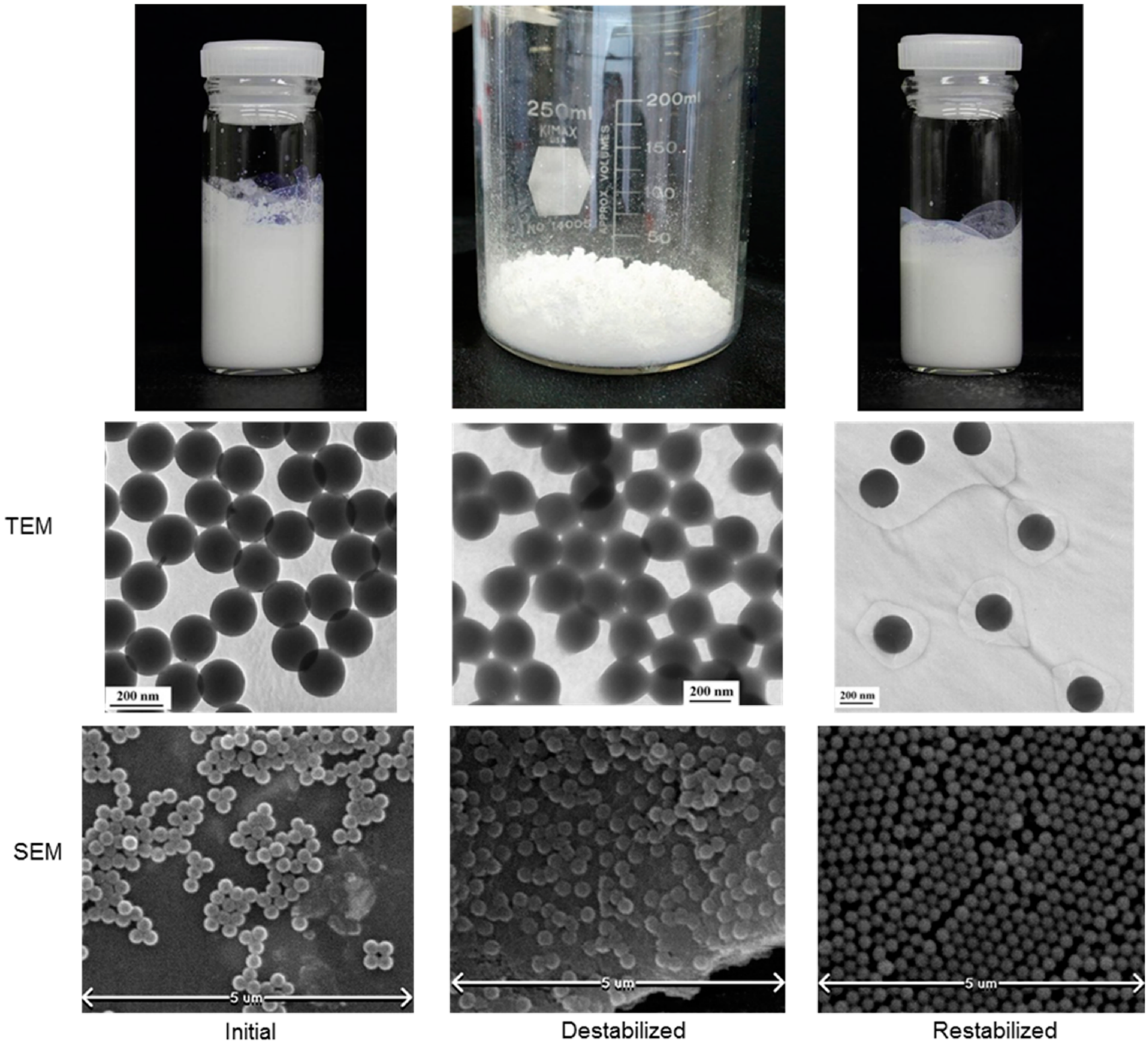


Figure 1. Photographs and TEM and SEM micrographs of the original latex from entry 4 (left), after destabilization in the presence of poly(DEAEMA) (middle) and redispersed after 10 min of sonication under CO_2 atmosphere (right).

To increase the initiation efficiency toward styrene polymerization and therefore the rate of nucleation and the number of particles, 5% of the styrene was replaced by MMA (entry 3, Table 1). Because of its higher water solubility ($0.419\%_{mol}$[18]) as compared to styrene, MMA is expected to allow the formation of more hydrophobic oligomers in the aqueous phase and a lower amount of water-soluble oligomers. This experiment yielded a monomer conversion of 71% and the formation of a stable latex with monodispersed particles having a *Z*-average diameter of 300 nm. An increase in the amount of initiator (entries 4 and 5) then allowed monomer conversion to reach 90% while maintaining similar latex properties.

The latexes could be stored for weeks at room temperature while under a CO_2 atmosphere without showing any phase separation. Their characterization by DLS (Table 1), TEM, and SEM (Figure S1) confirmed the monodisperse character of the particles, which could also be noticed from the iridescence of the dried samples (Figure S2). The particle diameters were 230−300 nm depending on the monomer conversion. The narrow size distribution of particles can be explained by the formation of particles through a homogeneous nucleation process, as observed in other SFEP.[17,19−21]

The coagulation and redispersion of polymer latexes arising from entries 3−5 were then evaluated (Table 2). To achieve coagulation, the latexes were first subjected to air bubbling at 40 °C and for 30 min. While latexes from entries 3 and 4 could be easily coagulated, the latexes arising from entry 5 remained stable even after applying the procedure at 60 °C for 1 h (Figure S3). In addition, the size of the aggregates decreased with an increasing amount of initiator employed during the latex synthesis, in contrast to our previously reported observations concerning the aggregation behavior of latexes prepared with switchable surfactants.[5] Such differences in the coagulation behaviors of the latexes can thus be attributed to a decrease in the molecular weight of the water-soluble polymer formed in the initial stages of the polymerization. Indeed, it is probable that very short, water-soluble poly(DEAEMA$^+$HCO$_3$$^-$) chains present in the latex, when converted to their neutral form upon CO$_2$ removal, would adsorb at the surface of only one particle. On the other hand, longer chains would be able to adsorb at the surface of two or more particles, thus, inducing bridging flocculation and further favoring latex destabilization.

To confirm this hypothesis, a polymer latex having similar properties as the latex arising from entry 4 was prepared by SFEP in the absence of DEAEMA and with 0.15% of VA-061 (entry 6, Table 1). This new latex failed to destabilize when treated with air and, thus, behaved just as did the latex from entry 5 (0.25% of VA-061) and not like the similar latex arising from entry 4, which formed aggregates of 5.7 μm upon destabilization. Such behavior suggests that the coagulation behavior depends on the presence and molecular weight of the water-soluble polymer. An aqueous solution of poly(DEAEMA$^+$HCO$_3$$^-$) ($M_n$ = 27300 g·mol-1, $Đ$ = 3.2) was therefore prepared by dissolving 67 mg of poly(DEAEMA) (synthesized by free radical polymerization in carbonated water and further dried, as explained in the Supporting Information) in 2 mL of carbonated water. The polymer solution was then added to latex samples from entries 4−6 in order to match the DEAEMA concentration present in latex corresponding to entry 3. While no difference in viscosity or particle size could be observed after addition of the solution under a CO$_2$ atmosphere, an increase in the extent of destabilization and the size of the aggregates could be noticed when the samples were subjected to air bubbling at 40 °C for 30 min. In particular, the two latexes (entries 5 and 6, Table 2) that exhibited negligible destabilization in the absence of added poly(DEAEMA), produced aggregates greater than 35 μm. It is thus likely that poly(DEAEMA$^+$HCO$_3$$^-$) is acting as a nonionic polymer flocculant when converted to poly(DEAEMA). In contrast to the latex before the destabilization procedure that shows well-separated primary particles, the latex sample that has been destabilized by treatment with air and heat shows extensive aggregation, producing particles that are much larger than 1 μm. It is important to note that the primary particles, while they are touching each other in the aggregated form, remain spherical and do not fuse together (Figures 1 and S4).

Once destabilized, latexes 4−6 could be easily filtered and dried under vacuum overnight to produce dried polymer powders (Figure 1). The dried powders were then redispersed in carbonated water to the same solid content (27 wt %) by CO$_2$ bubbling followed by ultrasound (sonication bath) for 10 min. All polymer particles were well dispersed and restabilized as attested by the recovery of the original zeta-potential. A slight increase in the particle size determined by DLS has been noticed, suggesting that a few aggregates comprising 3 or 4 particles remained. Nevertheless, as confirmed by TEM and SEM (Figures 1 and S4), the poly(DEAEMA) film totally disappeared and most particles maintained their original size and shape. The ability of the polymer particles, prepared here by SFEP, to be redispersed from a dry-powder state to a well-defined and stable latex is here a strong improvement as compared to our previous results. Indeed, in the latter case, only destabilized latex solutions were able to be restabilized.

In summary, the surfactant-free polymerization of styrene/MMA (0.95/0.05) in the presence of small amounts (0.54%) of DEAEMA and under CO$_2$ atmosphere allows the production of well-defined latex from commercially available compounds. The product latex is CO$_2$ stimuli-responsive and can be easily aggregated/redispersed using only air or CO$_2$. Water-soluble poly(DEAEMA$^+$HCO$_3$$^-$) formed during the emulsion polymerization has been found to act as a CO$_2$-switchable-flocculant, allowing for a facile coagulation and redispersion process. Most importantly, even after being dried to a powder, the particles could be restabilized to restore the original latex. This facile and reversible flocculation may bring cost savings in the areas of separation, storage, and transportation which should benefit the environment. The influence of the amount of initiator and DEAEMA on the properties of the latexes, in terms of particle size and destabilization/redispersion behavior, is now under investigation. Broadening of the process to other monomers is also being explored.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and additional characterization results using SEM, TEM, and static light scattering (Malvern Mastersizer 2000). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from National Sciences and Engineering Research Council of Canada, the Ontario Research Chairs Program (Cunningham), the Killam Trusts (Jessop), and the Canada Research Chairs Program (Jessop) for financial support. We also thank Dr. Xiaohu Yan for TEM and SEM analysis.

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