Ambidextrous Surfactants for Water-Dispersible Polymer Powders from Dispersion Polymerization in Supercritical CO_2

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ABSTRACT: A new concept is introduced in which a surfactant, poly(dimethylsiloxane)-*b*-poly(methacrylic acid) (PDMS-*b*-PMA) (M_w = 5500 g/mol PDMS, 900 g/mol PMA), is utilized to stabilize an organic latex in either a nonpolar medium, dense CO_2, or water. The latex particles, in this case poly(methyl methacrylate) (PMMA), were synthesized by dispersion polymerization in supercritical carbon dioxide. In CO_2, the PDMS block provides steric stabilization while the PMA block adsorbs to the particle surface. Upon transfer to water, the PDMS block collapses onto the surface and the PMA block ionizes for pH > 5 to stabilize the latex by electrostatic repulsion, as shown by zeta potential measurements. The surfactant is "ambidextrous" in that it provides stabilization in either CO_2 or water, by different mechanisms in each medium. Smaller more uniform particles were produced in CO_2 with a mixture of the commercially available surfactant, PDMS-*g*-pyrrolidonecarboxylic acid (PDMS-*g*-PCA) (M_w = 8500 g/mol, ∼2 PCA groups) and PDMS-*b*-PMA.

Introduction

A dispersion polymerization is one in which the monomer and initiator are soluble in the reaction medium, while the polymer formed is insoluble.[1,2] A polymeric surfactant is used to sterically stabilize nucleated polymer particles and prevent flocculation and precipitation of the reaction product. Monodisperse or nearly monodisperse latex particles can be produced with diameters ranging from submicrons to tens of microns. Recent research has shown that supercritical carbon dioxide can be used as a solvent for dispersion polymerization of various monomers including styrene,[3] methyl methacrylate,[4] 2-ethylhexyl acrylate,[5] and vinyl acetate.[6] Poly(methyl methacrylate) and poly(vinyl acetate) particle formation mechanisms in CO_2 have been investigated in situ using high-pressure turbidimetry.[6,7] Carbon dioxide is nontoxic, nonflammable, inexpensive, and environmentally friendly, making it an attractive alternative to many organic solvents currently used for dispersion polymerization. Polymer particles can also easily be collected as dry, free-flowing powder by simply depressurizing the reactor, eliminating the need to evaporate large quantities of solvent.

The solvent properties of carbon dioxide are unlike both lipophilic and hydrophilic solvents. Carbon dioxide has a very low polarizability per volume and low dielectric constant, making its solvating power similar to that of a fluorocarbon oil. The key to dispersion polymerization in carbon dioxide has been the development of surfactants with a highly CO_2-soluble segment which can sterically stabilize the latexes that are formed.[8−11] These amphiphilic materials have a "CO_2-philic" group which is highly soluble in CO_2 and an "anchor" group which is adsorbed to the surface of the polymer particles. The "CO_2-philic" group extends out from the surface of the polymer particles into the CO_2 phase, acting as a steric barrier to prevent flocculation.[10,11] Because CO_2 has such weak van der Waals forces, low cohesive energy density polymers such as a poly(1,1-dihydroperfluorooctyl acrylate), poly(perfluoropropylene oxide), or poly(dimethylsiloxane) have been found to be effective "CO_2-philic" groups,[12−14] which is consistent with their high solubilities.[15] Since the surfactant remains on the surface of polymer particles produced by dispersion polymerization, it imparts a very hydrophobic coating. For certain applications in which water wettability or redispersion of the polymer particles to form an aqueous latex is desired, the hydrophobic surface may be undesirable.

In most studies of dispersion polymerization, the "anchor" group of the surfactant is composed of the same polymer produced by the reaction to ensure a favorable interaction between the "anchor" and the particle surface. A few studies have shown that chemically dissimilar anchor groups can be effective such as polystyrene anchors for the dispersion polymerization of methyl methacrylate[16] and poly(methyl methacrylate) as an anchor for vinyl acetate dispersion polymerization.[17] Barrett suggested that the success of a variety of "anchor" groups may be attributed to the fact that most anchor blocks or grafts have relatively low molecular weight, and the range of compatibility of polymers increases as molecular weight decreases.[1]

The objective of this study was to develop surfactants that can stabilize polymer particles produced by dispersion polymerization in CO_2 which can be transferred to water to form an aqueous latex. Here the surfactant "anchor" group was chosen to impart hydrophilic groups on the surface of the polymer particles. The concept is illustrated in Figure 1. Since the surfactant remains on the surface after polymerization in CO_2, it is expected that the presence of hydrophilic groups will increase water wettability. For poly(dimethyl siloxane)-*b*-poly(methacrylic acid) (PDMS-*b*-PMA), the hydrophilic anchor does not ionize in CO_2, and thus it is appreciably soluble. When the particles are transferred from CO_2 to buffered water, some of the methacrylic acid groups in the surfactant ionize to produce an electrostatically

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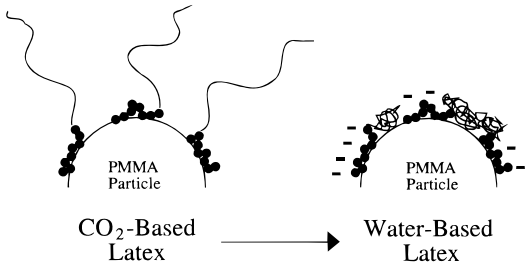

Figure 1. The "ambidextrous" surfactant concept is illustrated showing a single surfactant which can stabilize latex particles in supercritical CO_2 through steric stabilization and in water through electrostatic stabilization.

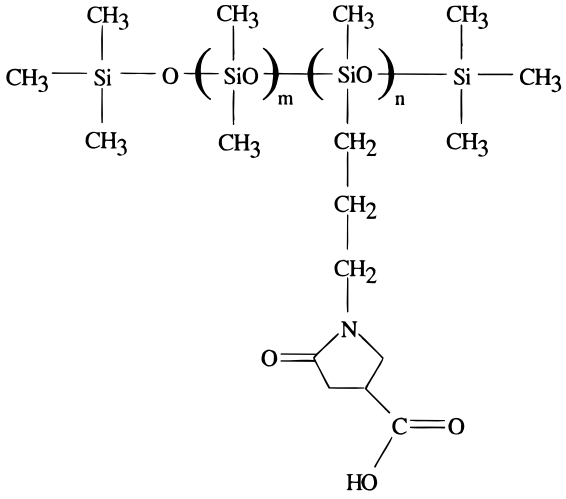

Figure 2. Structure of PDMS-*g*-PCA (Monasil PCA, Mona Industries). The total molecular weight is approximately 8500 g/mol with approximately two carboxylic acid groups per molecule.

stabilized latex. In water, the PDMS collapses onto the surface. To some extent the anchor block becomes the stabilizing block and vice versa. We refer to a surfactant that can stabilize particles in both CO_2 and water as "ambidextrous". It is ambidextrous in that stabilization is achieved in two very different types of interfaces. In this case, two different stabilization mechanisms are utilized. To our knowledge, the use of a single surfactant to transfer polymer particles from a nonpolar latex to a water-based latex has not been reported previously.

Water-dispersible polymer powders have a variety of applications and are typically produced by spray-drying an aqueous latex.[18,19] Redispersible polymer powders are industrially important as they allow latexes to be shipped at effectively 100% solids, eliminating the need to ship water. For latexes in carbon dioxide, drying large quantities of water is eliminated for isolating the polymer as a powder.

Experimental Section

Materials. The surfactants investigated were a poly(dimethylsiloxane)-*b*-poly(methacrylic acid) (PDMS-*b*-PMA) and a poly(dimethylsiloxane)-*g*-pyrrolidonecarboxylic acid (PDMS-*g*-PCA). The PDMS-*g*-PCA (commercial name Monasil PCA) was obtained from Mona Industries (Paterson, NJ) and used without further purification. The structure is shown in Figure 2. The molecular weight of approximately 8500 g/mol was determined by GPC after methylation of the carboxylic acid groups with diazomethane. From the NMR spectra and titration with methanolic potassium hydroxide in tetrahydrofuran (THF), there were approximately two pyrrolidone carboxylic acid groups per molecule.

For PDMS-*b*-PMA synthesis, THF was distilled from sodium naphthalide under reduced pressure prior to use. *tert*-Butyl methacrylate (tBMA) (Polysciences) was first distilled from CaH_2, followed by distillation from triethylaluminum.[20] The group transfer polymerization (GTP) catalyst, tetrabutylammonium bibenzoate (TBABB), was synthesized according to the procedure in the literature.[21] Poly(dimethylsiloxane) monomethacrylate (Aldrich, M_w = 11 000 g/mol), ethyl dimethylsilane (United), and tris(triphenylphosphine)rhodium(I) chloride (Wilkinson catalyst) were used as received.

For dispersion polymerizations in carbon dioxide, methyl methacrylate (MMA) (Aldrich, 99%) was passed through an alumina column (Aldrich) to remove inhibitor prior to use. Carbon dioxide (Praxair instrument grade, 99.99%, <15 ppm oxygen) was used without further purification. 2,2′-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was recrystallized from methanol prior to use.

Phosphate buffer solutions were prepared from 3 mM solutions of either sodium phosphate, monobasic monohydrate (J. T. Baker), or sodium phosphate, dibasic heptahydrate (Mallinckrodt). The pH was then titrated to 8.17 for the monobasic sodium phosphate and to 11.36 for the dibasic sodium phosphate by using sodium hydroxide (EM Science). Sodium chloride was added to both buffer solutions to maintain a constant ionic strength of 11.2 mM. The ionic strength of the buffers was calculated by using a published computer subroutine.[22]

Synthesis of PDMS-*b*-PMA. The GTP macroinitiator, a silyl ketene acetal functional PDMS, was prepared by reacting poly(dimethylsiloxane) monomethacrylate with a slight molar excess of ethyldimethylsilane in the presence of Wilkinson catalyst.[23] THF and 2 mol % TBABB (based on silyl ketene acetal functionality) were transferred into the reactor containing dried macroinitiator by means of a cannula. After 5 min of stirring, tBMA was added slowly via syringe, and the polymerization proceeded for 2 h under an argon atmosphere. The polymerization was quenched with degassed methanol (2 mL). After an additional half hour of stirring, THF and methanol were evaporated. The PDMS-*b*-poly(tBMA) copolymer was collected and dried at 10^{-3} Torr for 24 h.

The block copolymer was dissolved in dioxane (5 wt %), and *p*-toluenesulfonic acid (5 mol % relative to the PtBMA content) was added. After stirring for 12 h at 100 °C, the dioxane was evaporated. The hydrolyzed polymer was then dissolved in hexane and washed with water (pH 3). After evaporating the hexane, the polymer was dried in vacuo. The total molecular weight of the block copolymer was determined by GPC after methylation with diazomethane. Supercritical CO_2 extraction was used to separate homopolymer from similarly synthesized block copolymers.[24] It was found that 40% of the mass was homopolymer. The molecular weight ratio of the blocks was determined by NMR, assuming 40% of the mass was unconverted homopolymer. The final M_w was 5500 g/mol PDMS and 900 g/mol PMA. After hydrolysis, the average molecular weight of PDMS block had decreased (from 11K to 5.5K) by a redistribution reaction.[25] Thus, the polydispersity of the block copolymer increased due to the cleavage of the PDMS chain during hydrolysis. The polydispersity (M_w/M_n) was determined to be 1.62 by GPC. It was found that 90% of *tert*-butyl ester was converted to carboxylic acid by ^{1}H NMR analysis.

Dispersion Polymerizations in Carbon Dioxide. Dispersion polymerizations were conducted in a variable volume view cell as shown in Figure 3. The cell had a maximum volume of ~28 mL and was fitted with two sapphire windows $^5/_8$ in. in diameter and $^1/_8$ in. thick mounted perpendicular to the cell axis which allowed the contents of the reactor to be observed visually. The view cell could be turned horizontally, and a 1 in. diameter by 0.4 in. thick sapphire window allowed visual observations along the cell axis. Pressure was controlled with a computer-controlled syringe pump (ISCO, model 100DX) by using carbon dioxide as the pressurizing fluid. The cell was wrapped with heating tape and fiber glass insulation, and the temperature was controlled to ±0.5 °C.

The procedure for loading the reactor and conducting the polymerization has been discussed in previous papers.[7,26] All

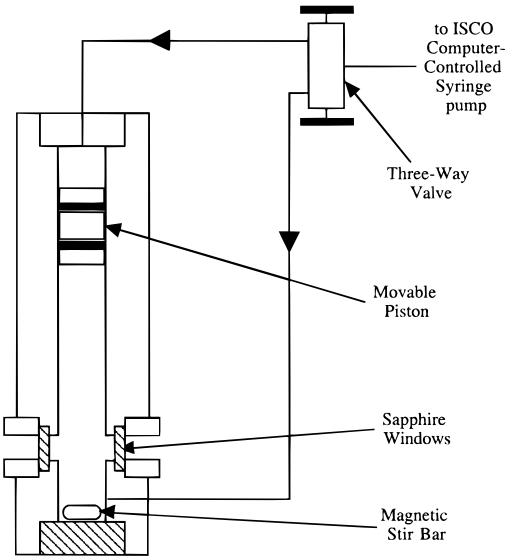

Figure 3. High-pressure dispersion polymerization apparatus.

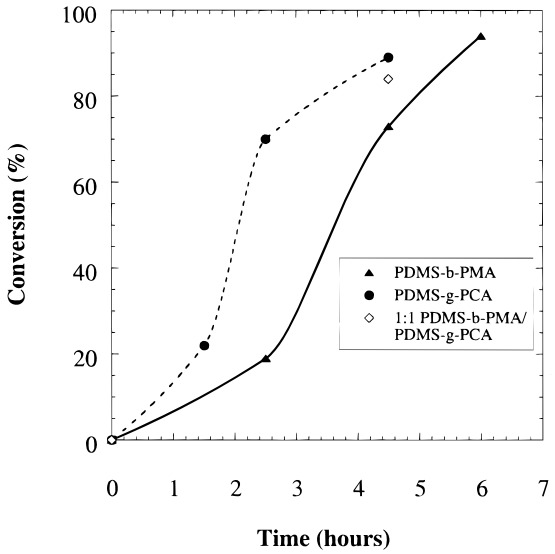

Figure 4. Conversion versus reaction time for methyl methacrylate dispersion polymerization in supercritical CO_2 with PDMS-*b*-PMA, PDMS-*g*-PCA, and a 1:1 mixture by weight of the two surfactants.

reactions were conducted at 345 bar and 65 °C with 16.4 wt % methyl methacrylate, 1.6 wt % surfactant (i.e., 10 wt % based on monomer), and 0.16 wt % AIBN (i.e., 1 wt % based on monomer). After the desired reaction time, the cell was turned horizontally and placed in an ice water bath for 15−20 min to quench the reaction while maintaining the cell at the reaction pressure. Residual monomer was extracted from the product by flowing approximately six residence volumes of CO_2 at ∼15 °C and 5000 psia, following the procedure of O'Neill.[26] The dry polymer powder was removed from the cell and weighed. Residual polymer was removed by dissolving it in tetrahydrofuran (THF) and placing into a tared vial. The THF was evaporated at ambient conditions in a fume hood. Remaining THF was removed by placing the vial in a 75 °C oven for ∼24 h. The conversion of the reaction was calculated by the weight of the final product divided by the weight of monomer added. A scanning electron microscope (Joel JSM-35C) was used to measure particle size of the latex particles.

Formation and Characterization of Aqueous Latexes. A 1 wt % aqueous latex was formed by adding 0.04 g of the dry polymer powder to 4 mL of buffer solution. The powder was dispersed into the buffer solution with an ultrasonic emulsifier (Branson Sonifier model 250D) at 30% of the maximum power for 5 min. Zeta potential measurements were conducted by using a microelectrophoresis apparatus (Komline-Sanderson Zeta-Reader, model ZR-12S). Measurements at pH 11.36 and 8.17 were made on separate latexes. The pH was lowered by adding drops of concentrated hydrochloric acid to the pH 8.17 latex. Zeta potential measurements in the buffered solutions were repeated four times at four different cell voltages (5, 10, 20, and 30 V/cm). No significant changes in measured zeta potential occurred as voltage was changed, and the reported zeta potential is the average of all 16 measurements. For pH lower than 8.17, an average of five measurements at 20 V/cm cell voltage are reported. Fewer measurements were taken at lower pH due to flocculation of the latex.

Dynamic light scattering (DLS) measurements were made using a Brookhaven Instruments particle sizer equipped with a BI-9000AT correlator. Two drops of the 1 wt % latex were added to 2 mL of buffer to dilute the sample. Scattering data were collected for 300 s, and measurements were repeated at least twice. The average diameter was calculated by using the method of cumulants.[27]

To compare the stability of the latexes to sedimentation, turbidity measurements at 650 nm were taken versus time with a Beckman DU-40 UV−vis spectrophotometer. For turbidity measurements, the 1 wt % latexes were diluted to 0.5 wt %. One milliliter of the 0.5 wt % latex was placed in a quartz cuvette with a 1 cm path length. The cuvette was positioned in the spectrophotometer so that the beam was focused ∼6.5 mm below the meniscus. Turbidty readings were taken until the turbidity had decreased 90% due to sedimentation of the latexes.

Results and Discussion

Reaction Kinetics and Product Morphology. Figure 4 shows the conversion versus time for all reactions. The shapes of the curves are similar to each other and those of previous reactions of methyl methacrylate in supercritical CO_2 with siloxane-based surfactants.[26] Initially, the reaction rate is slow as the polymerization occurs in the solution phase or in small particles that are highly plasticized by monomer and CO_2. As the locus of polymerization shifts to the interior of sterically stabilized latex particles, the diffusion of the active polymer chains becomes restricted due to chain entanglements, and the termination rate decreases. The resulting increase in the overall reaction rate is called the "gel effect" and is commonly observed in dispersion polymerization.[1] The gel effect has also been reported previously for the dispersion polymerization of MMA in supercritical CO_2.[12] While the shapes of the two curves shown in Figure 4 are similar, the reaction rate appears notably slower for the PDMS-*b*-PMA stabilized reaction than for PDMS-*g*-PCA, indicating a delay in the gel effect. Consistent with this delay, the molecular weight of the product produced with PDMS-*b*-PMA is also lower than that obtained with PDMS-*g*-PCA, as shown in Figure 5. The reaction conducted with the 1:1 mixture by weight of the two surfactants gives a conversion and molecular weight slightly lower than that of pure PDMS-*g*-PCA.

Scanning electron micrographs of the PMMA particles synthesized with PDMS-*b*-PMA are shown in Figure 6. The particles are initially stabilized by the surfactant but flocculate and coalesce as the reaction proceeds. The latex remained stable after 2.5 h, and particles removed from the reactor were unagglomerated as seen in Figure 6A. Flocculation of the latex eventually occurred, and the viscous settled latex could not be stirred after reacting for 4.5 h. The agglomeration of the individual

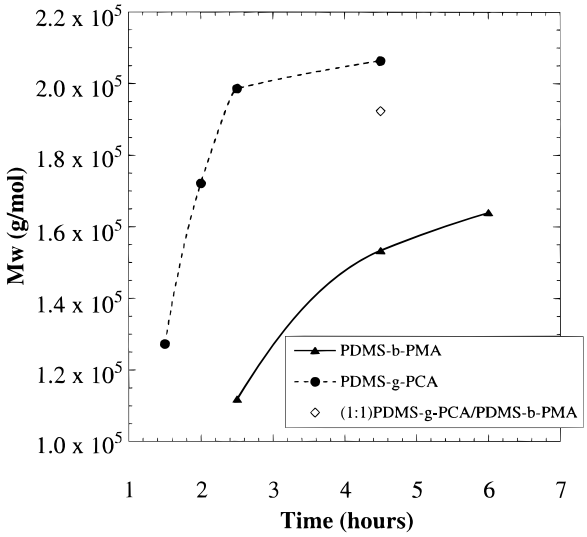

Figure 5. Weight-average molecular weight versus reaction time for methyl methacrylate dispersion polymerization in supercritical CO_2 with PDMS-*b*-PMA, PDMS-*g*-PCA, and a 1:1 mixture by weight of the two surfactants.

particles is clearly evident in Figure 6B,C. Both the anchor block and stabilizing block of PDMS-*b*-PMA are lower in molecular weight than those used previously for dispersion polymerization in supercritical CO_2.[28] The lower molecular weight of the anchor block was due to the low reactivity of *tert*-butyl methacrylate. The harsh conditions required to hydrolyze the *tert*-butyl methacrylate to methacrylic acid resulted in degradation of the PDMS molecular weight from 11 000 to 5500 g/mol. The low overall molecular weight of the surfactant may reduce anchoring to the surface of the polymer particles if the surfactant favors bulk CO_2 too strongly.[11] If the surfactant does not anchor quickly to the surface of the polymer particles, coagulation of the polymer nuclei can occur for a longer period of time in the early stages of the reaction, increasing both polydispersity and particle size. Also, the lower molecular weight of the stabilizing block may be insufficient to sterically stabilize the large particles which form since van der Waals attraction increases as particle size increases.

Figure 7 shows scanning electron micrographs of particles produced with PDMS-*g*-PCA at various reaction times. The particle size is quite uniform and increases with time as expected. At longer reaction times, the particles are somewhat agglomerated. The product collected after 1.5 h shows very little evidence of agglomeration while that collected after 2 h shows some fusion between particles. This agglomeration is consistent with visual observations of settling during reaction. After 1.5 h, the latex did not show any signs of sedimentation even after the stir bar was turned off for 1−2 min. At 2.0 h, the latex could be stirred easily but settled very quickly once the stir bar was turned off. Eventually, the latex could no longer be stirred, and the product was more agglomerated. The product collected after 4.5 h was agglomerated but was easily broken up into a free-flowing powder with a spatula as it was removed from the reactor.

Barrett has shown that the reaction rate and molecular weight decrease when flocculation occurs during dispersion polymerization of MMA in organic media.[29] A previous study of dispersion polymerization of MMA in supercritical CO_2 has shown that the reduction of surface area caused by flocculation can cause diffusional

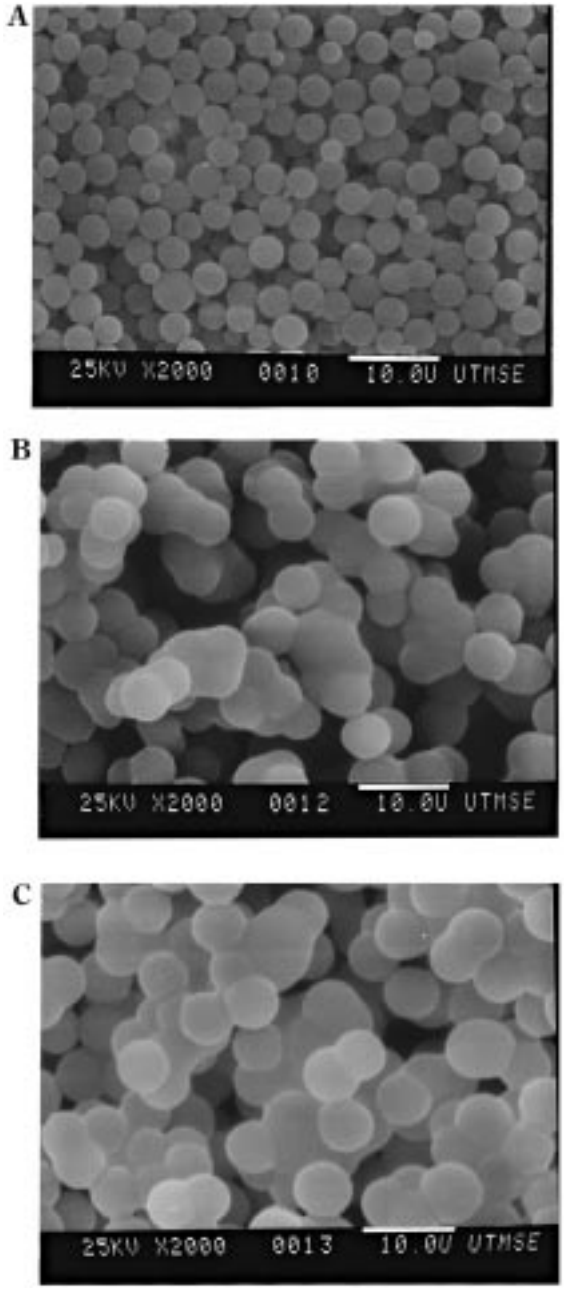

Figure 6. Scanning electron micrographs of poly(methyl methacrylate) particles produced with PDMS-*b*-PMA stabilizer after (A) 2.5, (B) 4.5, and (C) 6.0 h. All reactions conducted at 345 bar and 65 °C with 16.4 wt % MMA, 1.6 wt % PDMS-*b*-PMA, and 0.16 wt % AIBN.

restrictions of monomer into the agglomerated particles, resulting in an increased contribution of solution-phase polymerization and lower molecular weight product.[26] It is evident from Figures 6 and 7 that agglomeration of the particles is more predominant with the PDMS-*b*-PMA surfactant, which can explain the reduced reaction rate and molecular weight observed in Figures 4 and 5.

Poly(dimethylsiloxane) is significantly more soluble in supercritical CO_2/MMA mixtures than in pure CO_2.[26] The cosolvent effect of MMA increases the chain extension of PDMS which enhances steric stabilization. The particle morphologies observed in Figures 6 and 7 are consistent with the MMA cosolvent effect. The PDMS tail extension is reduced as the MMA is consumed by the reaction. Eventually, steric stabilization is lost as

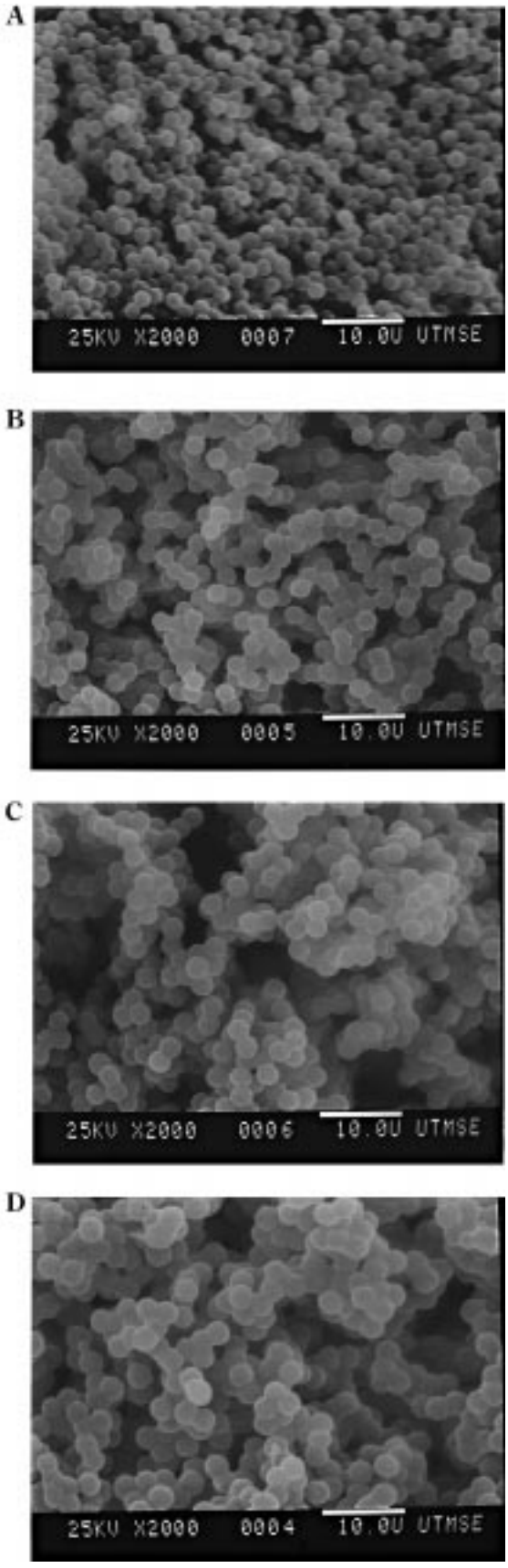

Figure 7. Scanning electron micrographs of poly(methyl methacrylate) particles produced with PDMS-*g*-PCA stabilizer after (A) 1.5, (B) 2.0, (C) 2.5, and (D) 4.5 h. All reactions conducted at 345 bar and 65 °C with 16.4 wt % MMA, 1.6 wt % PDMS-*g*-PCA, and 0.16 wt % AIBN.

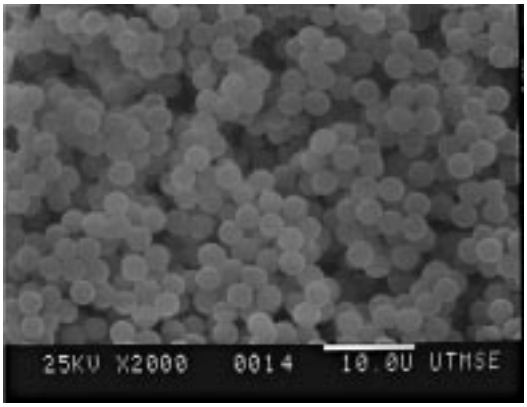

Figure 8. Scanning electron micrographs of poly(methyl methacrylate) particles produced with a surfactant mixture 1:1 by weight PDMS-*b*-PMA and PDMS-*g*-PCA after 4.5 h. Reaction was conducted at 345 bar and 65 °C with 16.4 wt % MMA, 1.6 wt % PDMS-*g*-PCA, and 0.16 wt % AIBN.

the chains collapse onto the surface of the polymer particles, and flocculation of the latex ensues.

The scanning electron micrograph of PMMA particles produced with the 1:1 by weight mixture of PDMS-*b*-PMA and PDMS-*g*-PCA after 4.5 h is shown in Figure 8. The particle size is only slightly larger than that obtained with pure PDMS-*g*-PCA. It was expected that the mixture of surfactants would produce particle sizes intermediate between those obtained with either pure surfactant. Surprisingly, however, the mixture of the two surfactants produces more monodisperse and less agglomerated particles than either individual surfactant. Since the PCA anchor groups are grafted at random locations along the PDMS chain in the PDMS-*g*-PCA surfactant, it is expected that the surfactant would be oriented closer to the surface. The overall molecular weight of PDMS-*g*-PCA is approximately 8500 g/mol. However, only the spaces between the PCA grafts are free to extend out from particle surface. Thus, the actual average length of PDMS extended from the surface may be only a fraction of the total length of the graft copolymer. The block copolymer PDMS-*b*-PMA is only anchored on one end, with allows the entire PDMS block to extend further out from the interface. From Figure 7, it appears that the PDMS-*g*-PCA surfactant adsorbs more strongly and thus more effectively prevents coagulation in the early stages of the reaction to produce smaller particles than the more weakly adsorbed PDMS-*b*-PMA produces alone. After this, the PDMS-*b*-PMA can adsorb and extend out farther from the interface to preserve the large number of small particles. Even with the mixture of the two surfactants, however, flocculation is not prevented completely. After reacting for 4.5 h, it is no longer possible to stir the settled latex in CO_2. The product is agglomerated but broken up easily into a free-flowing powder. The molecular weight and conversion obtained after 4.5 h are intermediate between those obtained with the two pure surfactants as seen in Figures 4 and 5 but are both closer to those obtained with pure PDMS-*g*-PCA. Since the particle size is closer to that obtained with pure PDMS-*g*-PCA, it is likely that solution polymerization and coagulation are minimized during the early stages of the reaction and that the gel effect begins near the point that it begins with pure PDMS-*g*-PCA.

Formation and Characterization of Aqueous Latexes. Attempts were made to disperse the dry polymer powder removed from the high-pressure reactor

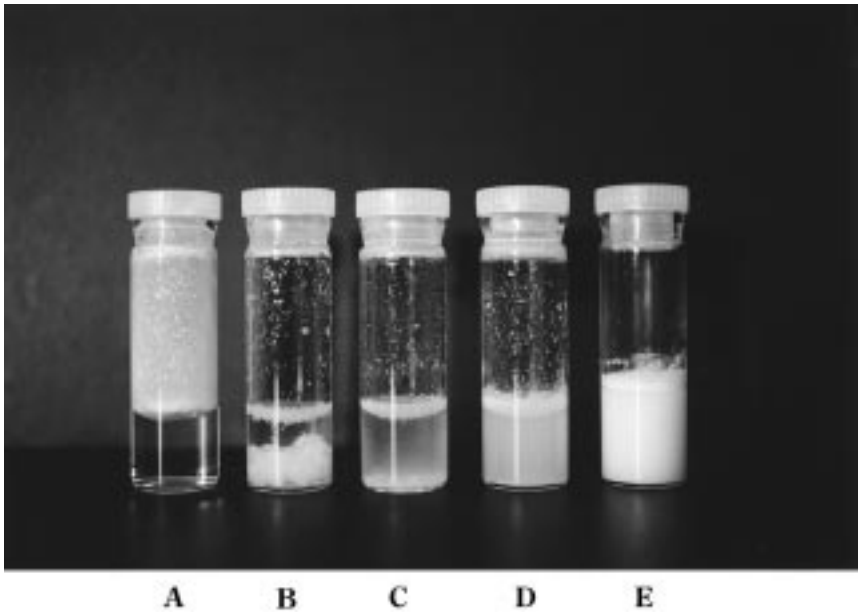

Figure 9. Picture of 1 wt % aqueous PMMA latexes formed in pH 8.17 phosphate buffer with particles produced by (A) PDMS macromonomer, (B) PDMS-*g*-PCA, (C) 1:1 by weight mixture of PDMS-*b*-PMA and PDMS-*g*-PCA, and (D) PDMS-*b*-PMA. Vial E is a 10 wt % latex of the particles produced with PDMS-*b*-PMA.

into aqueous buffer solutions by using an ultrasonic emulsifier. As a control, PMMA was also synthesized with a PDMS "macromonomer" (M_w = 11 000 g/mol) following the procedure given by O'Neill.[26] Figure 9 shows the appearance of latexes of 1 wt % in a pH 8.17 phosphate buffer after 5 min of sonification at 30% power. The latexes had a similar appearance in the pH 11.36 buffer. Vial A contains the PMMA particles synthesized with the PDMS macromonomer. As expected, since the surfactant contains no hydrophilic groups, the particles are very hydrophobic and cannot be dispersed into water. The particles were not even wetted by the water and attached to the sides of the vial. Vial B contains particles synthesized with pure PDMS-*g*-PCA with a 4.5 h reaction time. The PDMS-*g*-PCA particles could be wetted by water but remained as large flocs in the aqueous phase. The particles appeared to be partially dispersed during sonification but flocculated immediately afterward. Vial C contains particles synthesized with the 1:1 by weight mixture of PDMS-*g*-PCA and PDMS-*b*-PMA. These particles are nearly completely dispersed, but some small flocs remain visible. During sonification, the particles containing the mixture of the two surfactants appeared completely dispersed but partially flocculated afterward. Vial D contains the particles synthesized with PDMS-*b*-PMA with a 4.5 h reaction time. These particles were completely dispersed, and no flocs were visible. The particles synthesized with PDMS-*b*-PMA could be dispersed at least up to 10 wt % as shown in vial E. The latexes sedimented over time but could be completely redispersed with manual shaking even over 2 months after initially forming the latex.

Sedimentation curves were conducted on the pH 8.17 latexes formed with PDMS-*b*-PMA and are shown in Figure 10. The pH 11.36 latexes displayed similar sedimentation curves. These results are in qualitative agreement with the electron micrographs in Figure 6 which show that particle size increases with reaction time due to agglomeration of the particles. The larger agglomerates sediment more rapidly than the individual particles collected after 2.5 h. The sedimentation curves

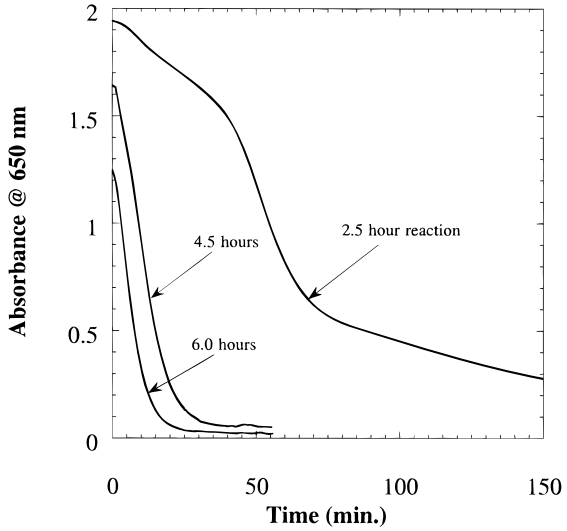

Figure 10. Turbidity versus time curves showing the stability to sedimentation of PMMA latexes produced with PDMS-*b*-PMA at various reaction times.

could be reproduced by redispersing the latexes with manual shaking.

The size of a spherical particle may be calculated from the sedimentation velocity according to Stokes' law:

$$D = 2\left(\frac{9\,\mu h}{2(\Delta\rho)gt}\right)^{1/2} \qquad (1)$$

where D is the particle diameter, μ is the viscosity, $\Delta\rho$ is the density difference between the particle and the dispersing medium, h is the sedimentation distance, and t is the sedimentation time. A sedimentation curve similar to Figure 10 was obtained for a 3.1 μm monodisperse polystyrene standard. This diameter was obtained from Stokes' law when the sedimentation time was defined as the time for the absorbance to decrease to 37% of its initial value. Thus, the average diameters of the PMMA latex particles were determined from the sedimentation curves by using this definition of sedimentation time.

Table 1. Particle Diameter (in microns) of Aqueous Latexes from Sedimentation and DLS Measurements Compared with Sizes of Dry Particles from SEM

reaction time (h)	SEM D_n (μm) (PDI)	sedimentation pH 8	sedimentation pH 11	DLS pH 8	DLS pH 11
2.5	3.37 (1.10)	3.8	3.7	2.6	2.2
4.5	8.06 (1.29)	8.3	9.1	7.1	6.7
6.0	9.66 (1.26)	10.6	9.8	8.3	9.2

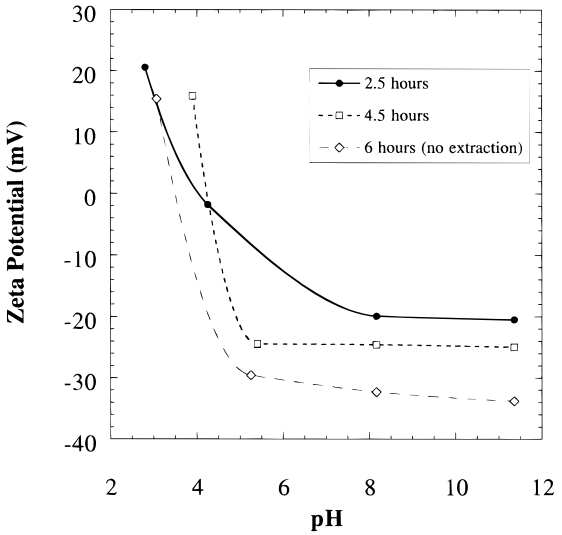

Figure 11. Zeta potential versus pH for PMMA latex particles synthesized with PDMS-*b*-PMA.

The particle size results from the scanning electron micrographs (SEM), DLS measurements, and sedimentation curves are summarized in Table 1. The average particle size was calculated from the scanning electron micrographs by measuring at least 120 particles. For the nonspherical agglomerated particles, the size was measured across the largest width. The SEM results also give the polydispersity index (PDI = D_w/D_n) in parentheses. The diameters calculated from the sedimentation curves are in good agreement with the average diameters from SEM micrographs. For the 2.5 h reaction, the average diameters are very near the weight-average diameter from SEM (3.7 μm). For the 4.5 and 6.0 h reactions, the average diameters calculated from the sedimentation curves are intermediate between the number-average and weight-average diameters determined from SEM analysis. The agreement is still notable considering that the particles from the 4.5 and 6.0 h reaction are mostly agglomerates which are not spherical in shape. Other geometries will sediment at different velocities depending on the friction factor.[30] DLS gives average diameters that are all lower than the number-average diameter from SEM. Sedimentation may be occurring during the DLS measurements, which could shift the measured size lower as larger particles settle faster than smaller ones. Also, DLS is most accurate for particles sizes 1 μm in diameter or less where biasing due to sedimentation is minimal.[31]

To characterize the surface charge of the latex particles, zeta potential measurements versus pH were conducted as shown in Figure 11. The negative zeta potential at pH 8.17 and 11.36 indicates that there are negatively charged surface groups due to the ionization of the methacrylic acid units of the PDMS-*b*-PMA surfactant. As the pH is lowered, a sharp increase in zeta potential occurs around pH 5. Similar results of zeta potential versus pH have been recently reported for carboxylic acid functionalized polypyrrole−silica microparticles,[32] where the increase in zeta potential was observed at a pH near the pK_a of the carboxylic acid groups (~4) as they were protonated. The pK_a of methacrylic acid is 4.65, and the pK_a of poly(methacrylic acid) is 5.65.[33] It has been reported that poly(methacrylic acid) in a linear block copolymer has the same pK_a as the PMA homopolymer.[34] Thus, it is likely that the pK_a of the poly(methacrylic acid) block in the PDMS-*b*-PMA surfactant lies between 4.65 and 5.65. The "elbow" observed in zeta potential versus pH occurs very near the expected pK_a of the methacrylic acid block. Thus, the zeta potential versus pH is consistent with protonation of methacrylic acid.

Nuclear magnetic resonance was used to determine the fraction of PDMS-*b*-PMA remaining on the latex particles produced in the 2.5, 4.5, and 6.0 h reactions. This fraction was found to be 0.04 g of surfactant/g of PMMA for all three reaction times. There were 0.10 g of surfactant/g of MMA added to the reactor. Since the latex particles settled to the bottom of the reactor, the top section contained surfactant that was not adsorbed to the particle surface. Nonadsorbed surfactant along with some residual PMMA was present after removing the latex particles from the reactor. THF was used to dissolve this residual material for NMR analysis. For the 6 h reaction, the residual material contained 0.25 g of surfactant/g of PMMA, confirming that there was a significant amount of nonadsorbed surfactant in the reactor.

For the 2.5 and 4.5 h reactions with PDMS-*b*-PMA, residual monomer was removed by extraction with CO_2. The extraction procedure could have removed some of the surfactant along with the monomer. After depressurization and removal of the latex particles, the residual material in the reactor contained 0.08 and 0.09 g of surfactant/g of PMMA for the 2.5 and 4.5 h reactions, respectively. The 6 h reaction, in which no extraction was done, contained 0.25 g of surfactant/g of PMMA in the residual material as stated above. However, the latex particles collected for all three reaction times contained the same percentage of surfactant. Clearly, extraction with CO_2 removes a significant amount of the nonadsorbed surfactant but appears to have little effect on the amount of surfactant remaining on the PMMA latex particles. It should also be noted that the nonadsorbed fraction should contain a higher percentage of homopolymer, since there is little driving force for adsorption of homopolymer.

The maximum surface charge density obtainable with the PDMS-*b*-PMA surfactant can be estimated by assuming that all of the surfactant is on the surface of the particles and that all of the methacrylic acid groups are ionized. For the 6 h reaction, 0.04 g of surfactant/g of PMMA remains. As much as 40% of this amount may be homopolymer, although the exact amount of adsorbed homopolymer is unknown. For the approximate calculation below, this amount was assumed. Using a particle size of approximately 9.7 μm (from SEM) and assuming a particle density of 1.0 g/cm^3, the number of PDMS-*b*-PMA chains per particle is calculated to be 1.08×10^9. From the molecular weight of the PMA block there are approximately nine ionizable groups per chain, assuming 90% hydrolysis. By multiplying the total number of ionic groups by the elementary charge and dividing by the surface area per particle, the maximum surface

charge density is 5.3 C/m^2. If there is less adsorbed homopolymer, the maximum surface charge density may be slightly higher.

The total charge enclosed by the surface of shear can be related to zeta potential by the following expression:[35]

$$q = 4\pi\epsilon\zeta R(1 + \kappa R) \quad (2)$$

where ϵ is dielectric permittivity, ζ is the zeta potential, R is the radius of the surface of shear, and κ is the inverse double-layer thickness. For water at 25 °C[35]

$$\kappa = 3.3 \times 10^9\sqrt{I} \quad (3)$$

where I is the ionic strength in mol/L and κ is given in m^{-1}. The dielectric permittivity of water at 25 °C is 6.95 $\times$ 10^{-10} C^2/(J m).[36] If it is assumed that the surface of shear is at the particle surface, then R = 4.85 μm for the PMMA particles produced by the 6 h reaction. The ionic strength of the pH 11.36 buffer is 0.0112 mol/L, and the measured zeta potential of the PMMA particles in the pH 11.36 buffer is −0.0338 V. By substituting these values into eqs 2 and 3, the total charge per particle is 2.4 $\times$ 10^{-12} C. Dividing by the surface area gives a charge density of 8.2 $\times$ 10^{-3} C/m^2, which is in the range of latex surface charge densities obtained by emulsion polymerization in water.[37] However, the electrokinetic charge density is 3 orders of magnitude lower than the calculated maximum surface charge density based upon the total number of methacrylic acid groups present.

Equation 2 is derived assuming that ideal Huckel conditions apply, so that the slipping surface is located at the particle surface. It is also derived for spherical particles, which is not the case for the particle agglomerates. Since ideal Huckel conditions do not apply, it is expected that the slipping plane will be located some distance from the surface, and the calculated charge density will be lower than the actual surface charge density. Equation 2 has been applied to calculate the surface charge density of egg albumin protein and gave results within a factor of 2 of the actual surface charge density.[30] To explain the 3 orders of magnitude difference between the maximum charge density and the charge density calculated from the zeta potential, the fraction of the ionized methacrylic acid groups on the PMMA particles would have to be small. It is possible that some of the PMA groups are inside the PMMA particle or are covered by the PDMS block and thus shielded from the buffer solution.

If all of the surfactant molecules were located on the surface and the particles contained 0.024 g of PDMS-*b*-PMA/g of PMMA (from NMR), the calculated area occupied per chain would be 0.274 nm^2. As a comparison, the area occupied per chain ranged from 30 to 51 nm^2 for poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (MW = 15K) onto silica according to measurements by ellipsometry.[38] Since the calculated maximum surface coverage is much higher than commonly seen with polymeric surfactants, it is likely that a significant fraction of the surfactant was not located on the surface and may have been buried inside of the particle or adsorbed in multiple layers. A very high surface coverage would affect the degree of ionization of the methacrylic acid. A mean-field theory of ionizable polymer brushes predicts that the degree of ionization decreases when the ionizable chains are packed closer together.[39] In our case, the low dielectric PDMS layer would further reduce ionization by shielding the PMA block from the buffer solution. Because ion dissociation can change by orders of magnitude with a change in dielectric constant from 80 to 2.5, the dielectric constant of PDMS, it is possible that a large fraction of surfactant was on the PMMA surface, in the protonated form. A more detailed analysis of surfactant surface coverage and surface charge density is needed to determine the fraction of un-ionized or shielded methacrylic acid groups remaining on the surface. Future work will focus on the development of higher molecular weight surfactants which can control agglomeration more effectively and produce smaller particles.

Conclusions

Water-dispersible polymer powders have been synthesized in supercritical CO_2 by using novel "ambidextrous" CO_2-philic/hydrophilic surfactants. The concept of using a single surfactant to both sterically stabilize particles produced during dispersion polymerization in a nonpolar medium and to electrostatically stabilize the particles when transferred to water has been demonstrated. Poly(methyl methacrylate) particles synthesized in CO_2 with PDMS(5.5K)-*b*-PMA(0.9K) surfactant formed an electrostatically stabilized latex at concentrations at least up to 10 wt % when dispersed into buffered solutions of pH 8 and 11. The resulting latexes sedimented 6.5 mm in times ranging from approximately 8 to 69 min depending on the particle size but were easily redispersed with manual shaking even 2 months after initially forming the latex. Zeta potential measurements showed that the particles were negatively charged at a pH higher than approximately 5. A rapid increase in zeta potential occurs near the pK_a of PMA as the pH is lowered, which is consistent with loss of ionization of surface methacrylic acid groups. The surface charge density calculated from the zeta potential was approximately 3 orders of magnitude lower than the estimated maximum surface charge density calculated from the total number of methacrylic acid groups present. The lower measured charge density suggests that a significant fraction of the methacrylic acid groups may not have ionized due to shielding or by being buried inside the PMMA particles.

The block copolymer PDMS(5.5K)-*b*-PMA(0.8K) produced particles several microns in diameter that flocculated and coalesced as the reaction proceeded, due to the low molecular weight of the PDMS tails. The final particle size in CO_2 or water was approximately 9−10 μm in diameter. PDMS-*g*-PCA produced smaller, more uniform particles (∼3 μm) in CO_2. However, the particles synthesized with PDMS-*g*-PCA rapidly flocculated when dispersed into aqueous buffer solutions due to insufficient electrostatic stabilization. The PDMS-*g*-PCA contained approximately two ionizable groups per chain compared to nine in the PDMS-*b*-PMA surfactant. A mixture of PDMS-*b*-PMA and PDMS-*g*-PCA produced much more uniform and less agglomerated particles than either surfactant alone in CO_2. The particles produced with the surfactant mixture showed improved water dispersibility over those synthesized with PDMS-*g*-PCA alone but were partially flocculated. The flocs were larger and sedimented faster than the particles formed with PDMS-*b*-PMA alone.

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