Trifunctional Ambidextrous Surfactants for Latexes in Supercritical CO_2 and Water

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ABSTRACT: Trifunctional poly(dimethylsiloxane) (PDMS) block copolymers PDMS-*b*-poly(*tert*-butyl acrylate (tBA)-*co*-acrylic acid (AA)), PDMS-*b*-poly(methyl methacrylate), PMMA-*b*-PAA, and PDMS-*b*-P(MMA-*co*-methyacrylic acid (MA)) were synthesized and utilized to stabilize PMMA latexes in both nonpolar (CO_2) and polar (water) solvents. Submicron PMMA particles synthesized by dispersion polymerization in supercritical CO_2 have been redispersed to form up to 40 wt % stable aqueous latexes. In CO_2, the PDMS block provides steric stabilization. Upon transfer to water, the MA or AA groups ionize producing electrostatic stabilization, while the acrylate group anchors to the PMMA polymer surface. In both media, the particle size remained constant, indicating good stabilization without agglomeration. The surfactant is "ambidextrous" in that stabilization is achieved in both CO_2 and water and by different mechanisms in each medium. PMMA particles stabilized with a PDMS macromonomer could be transferred to an aqueous solution of sodium dodecyl sulfate in water to produce a stable latex.

Introduction

Carbon dioxide is a nonflammable, essentially nontoxic, and environmentally benign replacement for organic solvents and water for minimization of waste.[1,2] Since CO_2 is nonpolar (unlike water) and has weak van der Waals forces (unlike lipophilic phases), it may be considered to be a third type of condensed phase. Because of its unusual properties and high compressibility, novel types of surfactant architectures are required to adsorb at CO_2-based interfaces. For example, surfactants have been designed to form reverse micelles in CO_2,[3−6] water/CO_2 microemulsions[7] and emulsions,[8] and organic/CO_2 latexes.[9] The fact that CO_2 is unlike both water and lipophilic organic phases opens up many interesting new possibilities in combinations of interfaces. In this study we design a new type of surfactant that can stabilize both organic/CO_2 and organic/water latexes.

Dispersion polymerization of various monomers, e.g., methyl methacrylate and styrene,[9−12] has been conducted in CO_2 to obtain particles with diameters from 0.1 to 10 μm. In dispersion polymerization, the monomer and initiator are both soluble in the continuous phase, and a surfactant is used to control the morphology of the particles that nucleate during the reaction.[13,14] Fluorocarbon- or siloxane-based homopolymers and copolymers have been developed as CO_2-soluble surfactants to stabilize these polymer latexes.[15−21] The "CO_2-philic" groups extend into the medium acting as steric barriers to minimize flocculation. For poly(1,1-dihydroperfluorooctyl acrylate) (PFOA)-based block copolymer stabilizers, the critical flocculation density, above which the latexes are stable, coincides with the theta density for the bulk PFOA−CO_2 system according to light scattering measurements[22] and Monte Carlo computer simulation.[18]

Recently, we demonstrated the concept of an "ambidextrous" surfactant which is active at both an organic−CO_2 interface and also at an organic−water interface as shown in Figure 1.[23] One of the surfactants was poly(dimethylsiloxane)-*b*-poly(methacrylic acid) (PDMS-*b*-PMA). In CO_2, PMMA particles are sterically stabilized by the PDMS segments. The hydrophilic anchor group, PMA, does not ionize in CO_2, and thus the surfactant is appreciably soluble, e.g. 1.5 wt % in pure CO_2 at 65 °C and 345 bar. Upon transferring the surfactant-coated particles to water (or buffered water), the PDMS block collapses onto the latex surface, and some of the PMA groups are ionized, producing electrostatic stabilization. In essence, 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 it stabilizes two different types of interfaces, each by a different stabilization mechanism. To our knowledge, the use of a single surfactant to transfer polymer particles from a nonpolar solvent (in this case CO_2) to water has not been reported previously.

With PDMS-*b*-PMA, up to 10% (w/w) PMMA dry powder was redispersed to form an aqueous latex. This powder was produced in CO_2 by dispersion polymerization. After 4.5 h of reaction, the particles agglomerated, and the resulting viscous latex, composed of particles about 8 μm in diameter, could not be stirred.[23] Although these particles could be dispersed in water, they settled in less than 1 h due to their large size. The agglomeration may indicate that the molecular weight of PDMS tail, 5500 g/mol, was not high enough to provide sufficient steric stabilization or that the anchor group, PMA, did not adsorb strongly enough on PMMA for sufficient surface coverage.

The objective of this study was to synthesize new ambidextrous surfactants that adsorb more strongly to PMMA, while providing sufficient steric stabilization to produce submicron latex particles in CO_2. The length

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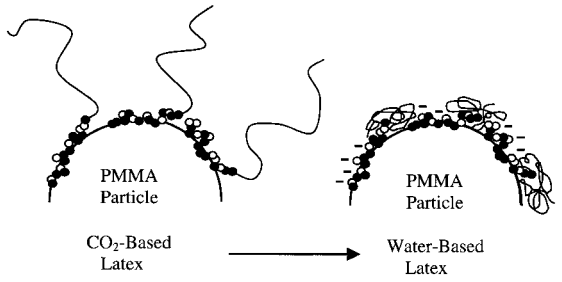

Figure 1. Ambidextrous surfactants for stable organic latex in either CO_2 or water with trifunctional copolymer: CO_2-soluble group (—), anchor group (●), and hydrophilic ionizable group (○).

of the PDMS block is varied to manipulate the thickness of the steric layer. Since the polar block PMA is not a good anchor group for the PMMA surface, another functionality was added to the surfactant to form a trifunctional surfactant, in this case methyl methacrylate (MMA) or *tert*-butyl acrylate (tBA). Thus, two CO_2-phobic blocks are present, MMA in order to anchor the surfactant to the PMMA surface and PMA or PAA to provide electrostratic stabilization upon transfer to water as shown in Figure 1. The molecular weights of the anchor block and CO_2-soluble block were controlled to attempt to obtain an appropriate anchor-soluble balance (ASB) for stable submicron latexes in CO_2, while also achieving stable concentrated latexes in aqueous media.

The Results and Discussion section begins with characterization of the latexes (yield, M_w, stability, morphology) produced by dispersion polymerization in CO_2 as a function of surfactant structure and adsorption. In the second part, the particle sizes of the aqueous latexes are compared with those for the CO_2 latexes. The stability is characterized in terms of the particle size and surface charge density, determined from the zeta potential. Most of the experiments were performed with ambidextrous surfactants. In the last set of experiments, a PMMA latex stabilized in CO_2 with a macromonomer was transferred to an aqueous solution of sodium dodecyl sulfate to achieve electrostatic stabilization.

This approach overcomes important drawbacks in the use of aqueous latexes: the need to ship large quantities of water and degradation due to freezing in cold climates. In the proposed process, the polymerization is carried out in CO_2 without producing wastewater, and then the dry powder is recovered simply by expanding the CO_2. The energy requirements are far less than in spray drying of an aqueous latex. The powder may be shipped to another location and redispersed in water or CO_2 and sprayed to form a coating. At the interface with air, the extremely hydrophobic PDMS groups provide a desirable low surface energy water-resistant layer. It is likely that a number of practical applications, e.g., coatings, adhesives, and drug delivery systems, may be developed given the ability of these surfactants to stabilize colloids in both CO_2 and water.

Experimental Section

Materials. For surfactant syntheses, tetrahydrofuran (THF) was distilled from sodium naphthalide under reduced pressure prior to use. Methyl methacrylate (MMA) (Aldrich), *tert*-butyl acrylate (tBA) (Polyscience), and trimethylsilyl methacrylate (TMSMA) (Aldrich) were first distilled from CaH_2, followed by distillation from triethylaluminum.[24]

The group transfer polymerization (GTP) catalyst, tetrabutylammonium bibenzoate (TBABB), was synthesized according to literature procedures.[25] Poly(dimethylsiloxane) monomethacrylate (Aldrich, M_n = 10 000 g/mol; Gelest, M_n = 5000 g/mol) was degassed under high vacuum for 2 days before use. Ethyldimethylsilane (United), acrylic acid (Aldrich), *N*,*N*-dimethylaniline (Adrich), trimethylsilyl chloride (TMSCl) (Aldrich), and tris(triphenylphosphine)rhodium(I) chloride (Wilkinson catalyst) (Aldrich) were used as received. GTP macroinitiator, the silyl ketene acetal functional PDMS, and trimethylsilyl acrylate (TMSA) were prepared as previously described.[26]

For dispersion polymerization in supercritical CO_2, purification of monomer and initiator has been described previously.[23] Carbon dioxide (Praxair instrument grade, 99.99%, <15 ppm oxygen) was used without further purification. Phosphate buffer solutions were prepared as described previously.[23]

Preparation of PDMS-*b*-PMMA-*b*-PAA Triblock Copolymer. THF (20 mL) and TBABB (7 mg) were transferred to a 100 mL flask containing the GTP macroinitiator (7 g) by means of a cannula. After 10 min of stirring, MMA (0.75 g) was added slowly via syringe. The polymerization proceeded for 1 h under argon atmosphere after which TMSA (1.5 g) was syringed into the reactor. The reaction was quenched with degassed methanol (2 mL) after 2 h. THF and methanol were removed by rotary evaporation. The polymer was collected and dried at 10^{-3} Torr for 24 h. All of the remaining solvents and monomers were removed. The final product contained about 30−40% unconverted PDMS−macromonomer and ca. 1000 ppm of catalyst. The hydrolysis of the TMSA block to PAA proceeded slowly as the sample was left in the air. Nuclear magnetic resonance (NMR) analysis confirmed that hydrolysis was almost complete after 1 week.

Preparation of PDMS-*b*-P(tBA-*co*-AA) and PDMS-*b*-P(MMA-*co*-MA). THF (20 mL) and TBABB (7 mg) were transferred to a flask containing GTP macroinitiator (7 g) by means of cannula. After 10 min of stirring, a mixture of tBA (0.8 g) and TMSA (0.6 g) (or a mixture of MMA (0.94 g) and TMSMA (0.98 g) as monomers for synthesis PDMS-*b*-P(MMA-*co*-MA)) was added slowly via syringe, and the polymerization proceeded for 2 h under argon. The rest of the procedure was the same as above.

Surfactant Characterization. Size exclusion chromatography (SEC) was carried out with a Waters GPC 510 apparatus equipped with a series of 5 μm linear, 10 nm, and 50 nm columns (American Polymer Standards Co.) to determine the molecular weight distribution of the copolymers. Polystyrene standards were used for calibration, and THF was used as the eluent. The molecular weight of each block was determined by ^{1}H NMR using a Varian Unity Plus-300. The molecular weight and polydispersity of the surfactants are listed in Table 1.

The composition and degree of hydrolysis were determined by ^{1}H NMR. The degree of hydrolysis and neutralization were determined by titration with 0.1 N KOH/MeOH in THF solution by using phenolphthalein as an indicator.

Dispersion Polymerizations in Supercritical CO_2. Dispersion polymerizations were carried out in a high-pressure apparatus including a volume variable cell as described earlier.[23,27,28] All the reactions were conducted at 65 °C and 345 bar with 1% (w/w) AIBN/MMA. The concentrations varied from 10 to 20% (w/w) MMA/CO_2 and 3−6% (w/w) surfactant/MMA. After a desired reaction time, the cell was placed in ice water to quench the reaction. The cell was turned to a vertical orientation, and the residual monomer was displaced from the reactor by flowing approximately 120 mL of CO_2 at 10 °C and 345 bar. The low temperature minimized the risk of coalescence due to plasticization of the polymer by CO_2. The CO_2 was vented from the top of the cell as a gas.

Formation and Characterization of Aqueous Latexes. Aqueous latexes were prepared by adding weighed amounts of dry polymer powder sequentially to buffer solution. The powder was redispersed with an ultrasonic emulsifier (Brabson Sonifier model 250D) at 30% of the maximum power for 2−10 min.

Table 1. Surfactant Characterization

surfactant	M_n (g/mol)	M_w/M_n	homopolymer PDMS content (ca. %)
PDMS-*b*-P(tBA-*co*-AA)	10K-*b*-(0.8K-*co*−0.5K)	1.24	40
PDMS-*b*-PMMA-*b*-PAA	10K-*b*−1.5K-*b*−0.7K	1.20	40
PDMS-*b*-P(MMA-*co*-MA)	5k-*b*-(1.1K-*co*−0.5K)	1.17	30−40

Table 2. Characterization of PMMA Synthesized in Supercritical CO_2 at 65 °C and 345 bar with 1% (w/w) AIBN/MMA

surfactant (w/w)[a]	MMA % (w/w)	time (h)	yield (%)	M_w (kg/mol)	M_w/M_n
3% PDMS-*b*-P(tBA-*co*-AA)	10	4	80	127	2.0
3% PDMS-*b*-PMMA-*b*-PAA	20	6	88	190	2.2
6% PDMS-*b*-P(MMA-*co*-MA)	10	6	94	110	2.2

[a] Based on monomer. [b] Based on CO_2.

Dynamic light scattering (DLS) was employed to measure the particle size by using a Brookhaven Instrument particle sizer equipped with a BI-9000AT correlator. Two drops of the 1 wt % latex were added to 2 mL of buffer. Scattering data were collected for 300 s, and the average diameter was calculated by using the method of cumulants.[29] The measurements were made three times and averaged. Sedimentation velocity was measured for a 4 mL latex (1 wt %, pH 11.36) sample with a height of 25 mm. Zeta potential measurements were conducted with a microelectrophoresis apparatus (Komline-Sanderson Zeta-Reader, model ZR-12S) by diluting 4 mL of 1 wt % aqueous latex into 250 mL. Measurements were made on separate latexes at pH 11.36 and 8.17. Drops of concentrated hydrochloric acid were added to the pH 8.17 latex to lower the pH until the latex began to flocculate. Zeta potential measurement on each dispersion was repeated five times at three different cell voltages (10, 20, and 30 V/cm) to obtain the average value. The zeta potential varied less than ±5 mV as the cell voltage was changed.

Results and Discussion

CO_2 Latexes Produced by Dispersion Polymerization. The conversion versus reaction time at 345 bar and 65 °C is shown in Table 2. With the presence of PDMS-based surfactants, the polymerizations resulted in higher conversions, approximately 80%, compared with polymerizations conducted in the absence of surfactant. After 4 h reaction, the conversion was only 24% without surfactant.[21] These results compare favorably with the work of Hsiao[19] and Shaffer.[21]

GPC analysis of PMMA produced in CO_2 indicated high values of M_w up to 190 kg/mol with a polydispersity of about 2.0 as shown in Table 2. As the locus of polymerization shifts from the solution phase to the particle phase, the diffusion of the active polymer chains becomes restricted because of chain entanglement in the highly viscous polymer phase. Thus, the termination rate decreases, and a concurrent increase in polymer molecular weight occurs due to this gel effect.[13,19]

Scanning electron micrographs (SEM) of the PMMA particles at various reaction time are shown in Figures 2. During the first 2−3 h reaction, the latexes remained stable when the stirring was turned off. As the monomer was consumed at longer reaction times, the particles were observed to settle down to the bottom of the cell in minutes if the stirring was stopped. PDMS is significantly more soluble in supercritical CO_2/MMA mixtures than in pure CO_2.[27,30] The cosolvent effect of MMA increases the chain extension of PDMS and thus enhances steric stabilization. The extension of PDMS tails is reduced as MMA is consumed by the reaction, and the solvency of the CO_2/MMA mixture decreases. When the conversion is above 80%, the PDMS chains partially collapse onto the surface of the particles, reducing steric stabilization. Because of the loose flocculation between the primary particles due to van der Waals forces, the latex sediments rapidly if stirring is stopped. In contrast to our previous polymerization with the difunctional PDMS-*b*-PMA surfactant,[23] the latex can be stirred easily throughout the entire reaction, and no large flocs formed and settled to the bottom. After CO_2 and residual monomer were vented, the dry free-flowing powder collected from the cell did not show evidence of agglomeration according to SEM. The spherical particles were uniform in size. These results indicate that the surfactants are efficient in preventing agglomeration even though the solvation of the PDMS tail in CO_2 is not strong enough to prevent loose flocculation during polymerization.

As can be seen in Figure 2a, the particle size of PMMA synthesized with PDMS-*b*-P(tBA-*co*-AA) is larger than those synthesized with PDMS-*b*-PMMA-*b*-PAA and PDMS-*b*-P(MMA-*co*-MA). For a block copolymer stabilizer, an appropriate ASB is required to achieve adsorption and steric repulsion. Barrett has shown that there is an ideal range for the ASB of the stabilizer in a dispersion polymerization.[13] The combined molecular weight of the anchor block (1300 g/mol) in PDMS-*b*-P(tBA-*co*-AA) may be too low for sufficient adsorption to the surface of the polymer particles for high surface coverage. The surfactant is likely to favor bulk CO_2 strongly due to the 10 000 g/mol PDMS block.[18] With weak adsorption, the coagulation of the polymer nuclei can occur for a longer period of time before the surface of the nucleus is covered sufficiently well by surfactant. The larger particle size for this surfactant relative to the other two is likely due to this limited adsorption.

Figure 2b shows the particles collected after polymerization with the surfactant PDMS-*b*-PMMA-*b*-PAA, which contains more anchor segments (2200 g/mol). This higher ASB relative to PDMS-*b*-P(tBA-*co*-AA) is likely the cause of the decrease in particle size, due to higher surfactant adsorption. To reduce the particle size further, lower monomer concentration 10% (w/w) and 6% (w/w) PDMS-*b*-P(MMA-*co*-MA) with even larger ASB compared with the above two surfactants were used. Figure 2c shows the particles were uniformly in the size of 670 nm. Increasing the surfactant concentration can affect the particle size and size distribution[31] by increasing the surface coverage of the surfactant on the particles to reduce coagulation.

The results for these three surfactants suggest that acrylate units in either random copolymer anchors or block copolymer anchors provide sufficient surfactant adsorption to produce micron-sized latex particles. The size of the particles decreased as the ASB and the concentration of the surfactant increased.

These block copolymers contain anchor groups at only one end, allowing the entire PDMS block to extend out from the interface to facilitate steric stabilization. Steric stabilization will be sensitive to the length and solvation of the PDMS block, assuming that sufficient anchoring is present.[32] The SEM figures show that a 5000 g/mol

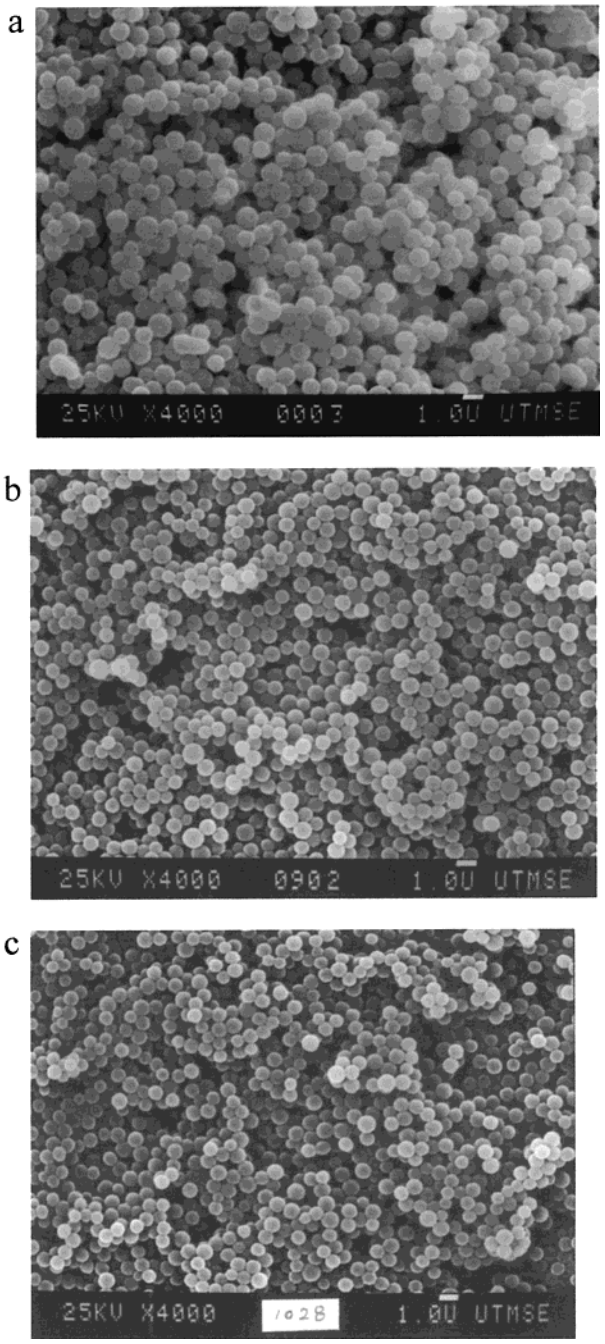

Figure 2. Scanning electron micrographs of poly(methyl methacrylate) particles produced with different surfactants: (a) PDMS-*b*-P(tBA-*co*-AA), (b) PDMS-*b*-PMMA-*b*-PAA, and (c) PDMS-*b*-P(MMA-*co*-MA). The reactions were conducted at 65 °C and 345 bar with the formulations in Table 2.

PDMS block is long enough to prevent agglomeration between the small particles. This molecular weight is significantly smaller than that in previous studies with PFOA- and PDMS-based stabilizers. However, the particles sedimented quickly in CO_2 if stirring was stopped at high conversions in all cases but did not sediment for low conversions. This loss of stability may be explained by a contraction of the PDMS tails as monomer is consumed, as the monomer acts as a cosolvent.[30]

According to neutron scattering studies, PDMS aggregates in CO_2 as the concentration increases above 0.01 g/mL.[33] Supercritical CO_2 appears to be a worse than Θ solvent for PDMS; thus, it is not surprising that the latexes underwent some flocculation as the monomer (cosolvent) was consumed.[34]

Table 3. PMMA Particle Diameter (in μm) in Aqueous Latexes Measured by DLS and the Sedimentation Velocity Compared with that of Dry Particles from SEM

surfactant	D_n (SEM)	D_w/D_n (SEM)	D (DLS)	D (sed.)
PDMS-*b*-P(tBA-*co*-AA) (10K-*b*-(0.8K-*co*−0.5K))	0.82	1.08	0.81	0.51
PDMS-*b*-PMMA-*b*-PAA (10K-*b*−1.5K-*b*−0.7K)	0.75	1.03	0.76	0.64
PDMS-*b*-P(MMA-*co*-MA) (5K-*b*-(1.1K-*co*−0.5K))	0.67	1.02	0.72	0.46

Table 4. Comparison of the PMMA Particle Size Produced with Different Surfactants in CO_2 at 65 °C and ∼345 bar after 4 h Reaction

surfactant (w/w)[a]	D_n (μm)	ref
PFOA (2.4−19%)	2.43−1.55	17
PDMS macromonomer (3.6−19%)	2.8−1.1	19
PDMS-*b*-polystyrene (10%)	0.23	33
P(MMA-*co*-HEMA)-*g*-PFPO[b] (15−22%)	0.8−2	18
PDMS-*b*-P(tBA-*co*-AA) (3%)	0.82	this work
PDMS-*b*-PMMA-*b*-PAA (3%)	0.75[c]	this work
PDMS-*b*-P(MMA-*co*-MA) (6%)	0.67[c]	this work

[a] Based on monomer. [b] Poly(methly methacrylate-*co*-hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide). [c] 6 h reaction.

The polymer product was redispered at a concentration of 2.5−5 wt % in pure CO_2 at 345 bar and 25−65 °C. The particles were stirred to form a white homogeneous latex that did not contain any large flocs, but it settled in a few minutes as the stirring was stopped. This result shows that a cosolvent is needed to produce sufficient solvation of PDMS tails in order to stabilize the latex for long periods.[30]

The particle size in CO_2 was calculated by averaging more than 300 single particles in the SEM pictures as listed in Table 3 in order to compare the results with those for the aqueous latexes. PDMS-*b*-P(MMA-*co*-MA) produced the least polydisperse (D_w/D_n) particles. These three surfactants produced much smaller particles than PDMS-*b*-PMA in CO_2 stabilized latexes studied previously.[23] Consequently, it should be easier to form stable latexes of these particles in water. The particle sizes are also compared with those in previous studies of dispersion polymerization using other stabilizers as shown in Table 4. The work by Hsiao et al.[19] and Shaffer and co-workers[21] showed that PFOA hompolymer and PDMS macromonomer led to particles in the size range from 1 to 2.5 μm. The use of graft or block copolymers stabilizers with anchor groups led to smaller particles, indicating better surface coverage.[20,35] The submicron particles in the present work were produced with much less surfactant than for the other copolymers in Table 4, indicating a desirable ASB and stabilizer block.

The adsorption of surfactant on the PMMA particle surface was measured by NMR as done previously.[23] After reaction, the monomer and free surfactant were displaced from the cell by flowing 120 mL of CO_2 at 3 mL/min and 345 bar through the vessel in a vertical orientation with the settled polymer particles resting on the bottom. This procedure is not expected to remove adsorbed surfactant from the particles.[23] Nonadsorbed surfactant was present along with some residual PMMA in the top section of the vertical cell and was not analyzed. The sample for ^{1}H NMR was collected from the bottom of the cell and used to determine the amount

Table 5. Adsorption of Surfactant on the Polymer Particles by NMR versus the Initial Ratio

surfactant	surf./PMMA (initial ratio)	surf./PMMA (NMR)	surf. coverage (nm^2)
PDMS-*b*-P(tBA-*co*-AA)	0.046	0.038	3.1
PDMS-*b*-PMMA-*b*-PAA	0.029	0.030	4.6
PDMS-*b*-P(MMA-*co*-MA)	0.076	0.071	1.2

of surfactant adsorbed to the polymer product. From the concentration ratio of methyl protons in dimethylsiloxane units to methyl protons in methyl methacrylate units, the amount of surfactant adsorbed per gram polymer was calculated. A correction was made for MMA groups in the surfactant when applicable. For comparison, the maximum possible ratio of surfactant to PMMA was evaluated from the amount of surfactant initially loaded and the polymer conversion. The results in Table 5 showed that for PDMS-*b*-PMMA-*b*-PAA and PDMS-*b*-P(MMA-*co*-MA) more than 80% of the surfactant was adsorbed. This value was only 60% for PDMS-*b*-PMA,[23] suggesting that the additional PMMA anchor group in the trifunctional surfactant enhanced the adsorption.

By assuming that all the surfactant molecules were located on the particle surface, the area per surfactant chain was calculated from the NMR spectra and the average particle size measured from SEM. The area/surfactant ranged from 1 to 5 nm^2. Dawkins and Taylor[36] measured the adsorption of polystyrene-*b*-PDMS (2400 to 48 000-*b*-11 200 g/mol) PMMA particles in hexane, and the area was 11−13 nm^2. The smaller area/surfactant in our study is consistent with the shorter block lengths. In our study, it is likely that part of the surfactant might have been buried inside the particles or have been present on the surface merely as a precipitate. Since the solvent THF dissolved all of the polymer and surfactant for the NMR measurement, it was not possible to determine the exact location of the surfactant with regard to the polymer surface.

Aqueous Latexes. An ultrasonic emulsifier was utilized to disperse dry polymer powder into buffer solutions. All the powders could be wetted and partially dispersed with manual shaking. A stable and completely dispersed latex was formed after a few minutes of sonication. No flocs were observed in the latex or on the wall of the vial. It was possible to form up to 40 wt % latexes by sonication for 20 min and adding drops of concentrated sodium hydroxide to a pH 11.36 buffer. A 30 wt % latex was stable at pH 8 for 6 h before a thin clear liquid layer appeared.

The aqueous latexes appeared to be very stable. The particles settled 25 mm after 36−270 h but could be completely redispersed with manual shaking. The redispersion could be achieved for over 3 months after initially forming the latex. The particle diameter, D, was calculated according to the following expression for hindered sedimentation of dilute monodisperse spheres[37]

$$D = 2\{4.5\mu u_s/((1-\phi)^n g\Delta\rho)\}^{1/2} \quad (1)$$

where u_s is the sedimentation velocity, μ is the viscosity of the suspension, ϕ is the volume fraction of the polymer, and $\Delta\rho$ is the density difference between the polymer and water. For a viscosity of the dilute dispersion of 1 cP, a polymer density of 1.188 g/cm^3,[38] and a correlation factor n of 6.55, the particle size for a 1 wt % latex ($\phi = 0.008$) was calculated (Table 3). It is likely that this method underestimated the particle size since the submicron particles settled very slowly, and there was not a sharp front between the clear water and the suspension. The predicted sizes were somewhat smaller than those determined by the other methods.

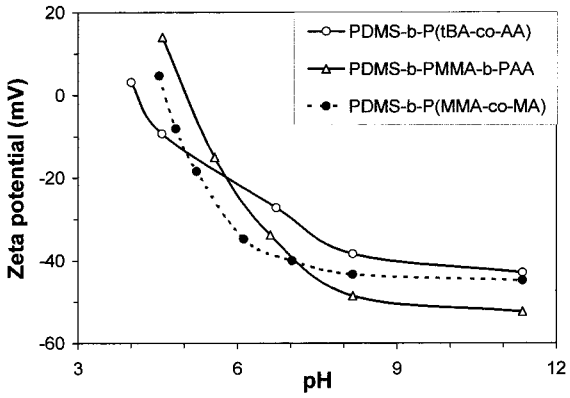

Figure 3. Zeta potential versus pH for PMMA latex particles synthesized with different surfactants.

Dynamic light scattering was used to measure the average particle size of the aqueous latexes as shown in Table 3. These values were in good agreement with those measured for dry polymer powder by SEM (after venting CO_2). This agreement indicates that the polymer did not flocculate upon transfer from CO_2 to water. The primary particles were stabilized electrostatically as the carboxylic acid groups ionized. Since the pK_a values of PMA and PAA are 5.65 and 4.75, respectively,[39] ionization may be expected in the pH 8.2 and 11.3 buffers.

Zeta potential measurements were used to determine the surface charge to explain the change in stability of the latexes with pH. The zeta potential versus pH is plotted in Figure 3 for an aqueous latex stabilized by the three ambidextrous surfactants. For a pH above about 8, the flat negative zeta potential indicates a constant degree of ionization of acrylic and methacrylic acid groups. As the pH is lowered by adding drops of hydrochloride acid to the pH 8.2 buffer, there is a sharp increase in zeta potential at a pH from 7 to 5. At the same time, flocs were observed in the latex, which indicated the electrostatic stabilization dissipated with the loss in surface charge. When pH was lowered further, the flocs grew and the zeta potential reached zero, indicating the ionization was completely suppressed. For water latex with surfactant PDMS-*b*-P(MMA-*co*-MA), the pH value at this point was 4.8, which lies between the pK_a values for the methacrylic acid monomer and PMA, 4.65 and 5.65, respectively.[39] With a molecular weight of only 500 g/mol for the methylacrylic acid segment, the point of zero charge was closer to the pK_a of the monomer than that of PMA. Zeta potential curves for the aqueous latexes containing the other two surfactants were consistent with the expected protonation behavior of the acrylic acid groups. The point of zero charge was located at pH 4.3 for PDMS-*b*-P(tBA-*co*-AA) and 4.6 for PDMS-*b*-PMMA-*b*-PAA. Both of these values fall between the pK_a values of acrylic acid and PAA, 4.20 and 4.75, respectively.[39]

The degree of ionization can be evaluated from the surface charge density on the particles. The theoretical maximum surface charge density was calculated from the adsorption data from NMR and the particle size in Table 3 by assuming that all the acid groups on the

Table 6. Surface Charge Density (SCD) Calculated from Zeta Potential Compared with the Maximum Possible Surface Charge Density on the PMMA Particles in pH 11.36 Aqueous Latex

surfactant	max SCD (C/m^2)	SCD (C/m^2)
PDMS-*b*-P(tBA-*co*-AA)	0.36	0.010
PDMS-*b*-PMMA-*b*-PAA	0.34	0.013
PDMS-*b*-P(MMA-*co*-MA)	0.79	0.011

surfactant were ionized. The total charge enclosed by the surface of shear can be related to the zeta potential according to the following expression:[40]

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

where ϵ is the dielectric constant, ζ is the zeta potential, R is the radius of the surface of shear, and κ is the inverse Debye length of the double layer. The value of ϵ for water at 25 °C is 6.95×10^{-10} C^2/(J m).[41] The surface of shear was assumed to be at the particle surface. For water at 25 °C[40]

$$\kappa = 3.3 \times 10^9 I^{1/2} \quad (3)$$

where κ is given in m^{-1} and I is the ionic strength of the solution in mol/L. For the pH 11.4 buffer, the ionic strength is 0.0112 mol/L. If it is assumed that the surface of shear is at the particle surface, then R is equal to half of the PMMA particle diameter from SEM. By substituting these values and the measured zeta potential into eqs 2 and 3, the total enclosed charge per particle was calculated. Dividing by the surface area gives a charge density of the magnitude 7.3×10^{-3} to 1.4×10^{-2} C/m^2, as shown in Table 6. This value is in the range of latex surface charge densities obtained by emulsion polymerization of styrene in water.[42]

In Table 6 the maximum theoretical surface charge is about 30−70 times greater than the surface charge calculated from zeta potential. It is likely that only a small fraction on the order of 1% of the acid groups close to the particle surface ionized. This type of behavior is commonly observed for polyelectrolytes at low dielectric constant surfaces in water. Some of the acid groups might have been buried inside the particles or covered by the collapsed PDMS chains. They may have been shielded from the buffer by a very low dielectric layer of polymer or PDMS blocks. The surface charge calculation from the zeta potential was based on the ideal Huckel assumption, where the surface of shear is located at the particle surface. This simple assumption leads to some uncertainty. When eq 2 was used to calculate the surface charge density for egg albumin protein with the Huckel assumption, the result was within the 60% of the actual surface charge density measured from titration.[43]

If the surface of shear is located at some distance away from the particle surface, eq 2 will predict a larger charge density. Yet the fraction of ionized groups would still be small since the magnitude of the zeta potential measured by electrophoresis is always smaller than the actual potential at the solid surface.[43] Even with a low degree of ionization, the aqueous latex was quite stable. In our previous work, the zeta potential indicated a surface charge density of only 8.2×10^{-3} C/m^2, corresponding to ionization of only 0.2% of the acid groups in PDMS-*b*-PMA.[23] With a higher charge density of $(1.1-1.3) \times 10^{-2}$ C/m^2 by using these trifunctional stabilizers, up to 40 wt % latexes have been formed, in contrast with only 10 wt % in the previous study.

In all of the above experiments stabilization was achieved in both CO_2 and water with a single surfactant. In the last set of experiments two separate commercial stabilizers were used. A stable latex was formed in CO_2 with PDMS macromonomer (M_n: 10 000) as described previously.[21,27,28] The CO_2 was vented to recover the particles. A 22 wt % latex was formed by redispersing the particles in a 1 wt % aqueous solution of sodium dodecyl sulfate (SDS). The latex was stable for 6 h in water. The favorable interactions between PDMS and the hydrocarbon tails of the SDS led to a coating of SDS on the outside of the particles. These results demonstrate that redispersion of latexes from CO_2 to water may be achieved with two separate stabilizers. An advantage of this process is that both of the stabilizers are commercially available.

Conclusions

Three types of trifunctional block copolymers containing PDMS CO_2-soluble blocks, acrylate anchor groups, and a PAA or PMA hydrophilic ionizable group were synthesized and utilized to stabilize PMMA latexes in both nonpolar (CO_2) and polar (aqueous) media. The surfactants are ambidextrous in that they stabilize latexes in both media and by different mechanisms in each case. In CO_2 the PDMS block provides steric stabilization and collapses upon transfer to water. In water, only about 1% of the AA or MA groups ionize, as determined from the zeta potential, yet this provides sufficient electrostatic stabilization. The change in surface charge with pH is consistent with the pK_a of the AA and MA groups. Upon transfer to water the particle size remained constant, indicating good stabilization in both media without agglomeration even for 40 wt % solids in water.

Submicron PMMA free-flowing particles with a narrow size distribution have been synthesized in CO_2. Despite the much smaller surfactant concentrations and lower molecular weight for the stabilizer block than in previous studies, submicron particles were produced indicating a desirable ASB. A M_n of only 5000 g/mol was sufficient to prevent agglomeration. The particle size decreased with an increase in the ASB for the surfactants studied. The particles were much smaller and less agglomerated than those produced with bifunctional PDMS-*b*-PMA ambidextrous surfactant, illustrating the advantage of adding a third block that anchors to the PMMA surface. Consequently, much more stable latexes were formed upon transfer to water.

Finally, latex particles synthesized in CO_2 that were stabilized by PDMS were redispersed in an aqueous solution of sodium dodecyl sulfate.

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