MATERIALS AND INTERFACES

Latexes Formed by Rapid Expansion of Polymer/CO₂ Suspensions into Water. 1. Hydrophilic Surfactant in Supercritical CO₂

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Rapid expansion of poly(2-ethylhexyl acrylate) suspensions in supercritical CO₂ containing a hydrophilic as well as a CO₂-philic surfactant produced stable aqueous latexes. The hydrophilic surfactants were soluble in both CO₂ and water. The aqueous latexes could also be formed after depressurization and resuspension of the polymer dispersion in CO₂. Latexes in basic buffer solutions were stable for a few weeks for concentrations up to 15.6% and for several months after sonication. The synthesis of water-dispersible polymer particles in CO₂, which may be transferred to water without the need for organic solvents, offers the possibility of new environmentally benign coatings and adhesives.

I. Introduction

Polymerization in supercritical carbon dioxide has received attention as an interesting alternative to conventional synthesis in water and organic solvents.[1−10] This approach minimizes wastewater and air pollution, because carbon dioxide is essentially nontoxic and environmentally benign. Other advantages of CO₂ include nonflammability, ease of separation from products, and low cost. However, because of its low dielectric constant, CO₂ is a poor solvent for polymers. Relatively few polymers are soluble in CO₂ without a cosolvent.[11−14] RESS of a crystalline fluoropolymer, poly(1,1,2,2-tetrahydroperfluorodecyl acrylate), which is highly soluble in carbon dioxide at temperatures near ambient, produces submicron to several micron-sized particles and fibers.[15] Polymers diluted with CO₂ have been sprayed for powder coating applications.[16]

Polymethacrylate latexes in CO₂ have been formed by dispersion polymerization with various macromonomer, homopolymer, and block copolymer stabilizers.[1,4−6,17−20] 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 (CO₂) and polar (water) solvents.[21] Submicron PMMA particles in supercritical CO₂ have been redispersed to form up to 40 wt % stable aqueous latexes. In CO₂, the PDMS block provides steric stabilization. Upon transfer to water, the MA or AA groups ionize, producing electrostatic stabilization, while the acrylate group anchors the stabilizer to the PMMA polymer surface in both media. The surfactant is "ambidextrous" in that stabilization is achieved in both CO₂ and water and by different mechanisms in each medium.

Considerable differences have been observed in dispersion polymerization for a polymer such as PMMA with a glass transition temperature, T_g, above 373.2 K versus a polymer with a low T_g, in our case 223.3 K. For high-T_g materials, polymer latexes with particle sizes in the 1 μm range are stable for hours without stirring. Low-T_g materials tend to produce larger particles during nucleation that are inherently more difficult to stabilize with surfactants.[3] The larger particle sizes have been confirmed by in-situ turbidimetric measurements for poly(vinyl acetate)[3] versus PMMA.[22] Suspensions of poly(2-ethylhexyl acrylate) (PEHA) in supercritical CO₂ formed by dispersion polymerization with a PDMS-based surfactant were sprayed to form uniform films.[9]

Products may be recovered from supercritical solution by rapid expansion to atmospheric pressure. Rapid expansion from supercritical CO₂ to organic liquid solutions has been used to form metal and semiconductor nanoparticles.[23] Stable suspensions of submicron particles of cyclosporine, a water-insoluble drug, have been produced by rapid expansion from supercritical to aqueous solution (RESAS).[24] In both of these cases a molecular solution is expanded into a liquid to produce submicron particles. In the present study, a suspension, rather than a solution, is expanded into water.

Our objective is to produce stable aqueous emulsions from PEHA suspensions in CO₂ without using an organic solvent or cosolvent. A CO₂-philic surfactant is utilized in dispersion polymerization to form a stable polymer suspension. A hydrophilic surfactant, which is soluble in CO₂, is also added to CO₂ to stabilize the suspension after it is transferred to water. The polymer suspensions in CO₂ are expanded rapidly into aqueous buffer solutions to produce polymer latexes. To our knowledge, the use of two surfactants, one hydrophilic and the other CO₂-philic, in the reaction followed by

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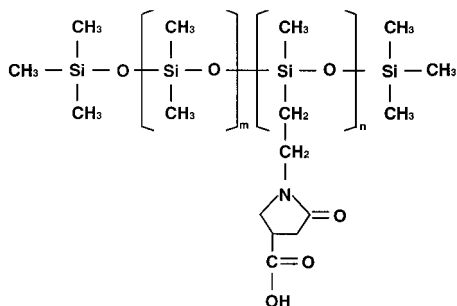
Figure 1. Molecular structure of Monasil PCA.

Table 1. Solubility of Surfactants in CO_2 and Water

surfactant	mol wt (g/gmol)	hydrophilic PEO/molecule (wt %)	solubility in CO_2 at 272.2 bar and 308.2 K (wt %)	in water at 296.2 K (g/100 g of water)
Monasil PCA	12100		1.0[a]	0.005
Pluronic L61	2210	10.9	0.8[b]	1.15
Pluronic L62	2460	19.9	0.2[b]	10.47
SAM 185	1620	40.7	0.1[b]	16.45

[a] Data from Calvo et al.[27] [b] Data from O'Neill et al.[28]

RESS of heterogeneous polymer suspensions to form aqueous polymer emulsions has not been reported yet. The use of two separate surfactants offers flexibility in designing emulsions in contrast with the use of a single ambidextrous surfactant.[20] In addition, commercial surfactants are available for this approach. The viscosity of high molecular weight PEHA containing dissolved CO_2 is too large for forming an aqueous emulsion by RESS as shown in this study. Instead of lowering the viscosity with an organic solvent, our approach is to reduce the viscosity by forming a suspension of small polymer droplets in CO_2. An emulsion in pure water or a basic buffer solution is then prepared by rapid expansion of the polymer suspension in supercritical CO_2. The buffer is used to reduce adhesion of the latex particles onto the glass surface of the container. The effects of surfactant structure, sonication, and basicity on the droplet size and stability of the PEHA emulsions in water are reported. With this concept, it is possible to produce latexes in CO_2 with minimal waste, which can be vented, shipped at low pressure, and resuspended in water or CO_2 to produce latexes for coatings and adhesives without organic solvent residues.

II. Experimental Section

Materials. 2-Ethylhexyl acrylate (2-EHA) with a purity of 98% was purchased from Aldrich Chemical. A CO_2-philic surfactant, Monasil PCA (PDMS-*g*-pyrrolidonecarboxylic acid), was obtained from Mona Industries. It has a CO_2-philic backbone and approximately two ionizable acid groups with a total molar mass of approximately 8500 (Figure 1). Hydrophilic surfactants composed of poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and/or poly(butylene oxide) (PBO), such as Pluronic L61 ($(PEO)_{2.7}(PPO)_{34.0}(PEO)_{2.7}$), Pluronic L62 ($(PEO)_{5.6}(PPO)_{34.0}(PEO)_{5.6}$), and SAM 185 ($(PBO)_{12}$-*b*-$(PEO)_{15}$), were chosen based on their relatively high solubility in both CO_2 and water (Table 1). The subscripts represent averages for these relatively polydisperse surfactants. These surfactants were obtained from BASF and were used without further purification. The initiator 2,2′-azobis(isobutyronitrile) (AIBN; Aldrich)
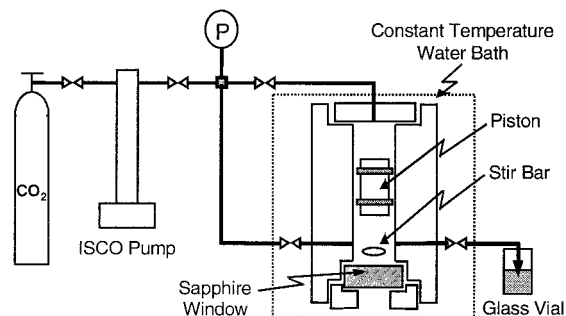

Figure 2. Schematic of the experimental apparatus for polymerization and RESS.

had a purity of 98% and was purified by recrystallization from methanol. The instrument-grade carbon dioxide (99.99% in purity) contained only trace amounts of impurities such as oxygen (<15 ppm) and moisture (<10 ppm). Research-grade tetrahydrofuran (THF) was used as received. The inhibitor was removed from the monomer as described in the literature.[8,9]

Basic 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 (EM Science) was added to both buffer solutions to maintain a constant ionic strength of 11.2 mM. Basic solutions were also prepared by dissolving known amounts of sodium hydroxide in water so that the pH values were 8 and 11.

Experimental Procedure. The experimental apparatus for the polymerization and RESS is shown in Figure 2. The variable-volume view cell with a piston was used as a polymerization reactor, and the reaction pressure was kept constant at 345 MPa with an ISCO model 100DX automatic syringe pump. The initiator, AIBN (1−2 wt %, w/w monomer); a CO_2-philic surfactant, Monasil PCA (2−5 wt %, w/w monomer); and a hydrophilic surfactant, Pluronic L61, Pluronic L62, or SAM 185 (3−11 wt %, w/w monomer), were charged into the cell, which was sealed and purged with CO_2. The monomer, 2-ethylhexyl acrylate, was then injected (usually 2−4 g), and a known amount of liquid CO_2 (5−10 times as much as the monomer) was pumped into the cell. The components were mixed together by a star head stir bar (Nalge, 14.3 mm in diameter), which was rotated vertically for 5 min. The reaction vessel was immersed horizontally into the water bath at 338.2 K controlled to within ±0.1 K. The polymerization reaction was maintained for about 6 h to obtain a high yield. For the polymerization with 5% Monasil PCA and 5% SAM 185, the yield was 98 ± 1%, a little bit lower than that with only Monasil PCA (99%).[9]

The stirred polymer suspension in the reaction vessel was expanded rapidly through a nozzle into water in a glass vial. The fused-silica capillary (100 µm i.d., Polymicro Technologies) was encased in poly(ether ether ketone) tubing (Supelco). All of the RESS experiments were performed while the suspension was held at 338.2 K, unless specified otherwise. Sonication was done by a Branson Sonifier 250 at an output level of 30% for 5 min. The molecular weight of the polymer was analyzed by gel permeation chromatography (Waters 510 GPC) with a refractive index detector and three AM GEL

Table 2. Dispersions of PEHA Formed in Either Water or Buffer Solution by Expanding through a Nozzle

surfactant in CO_2								
CO_2-philic (g/100 g of monomer)	hydrophilic (g/100 g of monomer)	polymer MW (g/mol)	liquid medium	polymer content in water (g/100 g)	visual quality[a] after shaking	particle size, original (μm)	particle size after sonication (μm)	sedimentation time after sonication (days)
Monasil (5.3)	Pluronic L61 (3.8)	123 000	water	0.13	fair	0.5		
		123 000	buffer at pH 11	0.10	good	2.3		
Monasil (5.0)	Pluronic L62 (5.3)	108 000	water	1.7	good	1.2	0.27	140
		108 000	buffer at pH 11	2.9	very good	1.6	0.33	135
Monasil (5.0)	SAM 185 (5.2)	112 000	water	15.6	good	2.7	0.34	
		112 000	buffer at pH 11	4.5	very good	2.4	0.34	

[a] Categories for visual observations of the latexes: fair, polymer adheres to the glass and small particles are visible in the latex; good, polymer adheres to the glass but discrete latex particles are not visible in the suspension, or particles do not adhere to the glass but small particles are visible; very good, polymer does not adhere to the glass and discrete latex particles are not visible in the suspension.

5-mm LIN silica gel columns (American Polymer Standards). THF was used as the solvent for the polymer. The signal was calibrated with the polystyrene standards. The molecular weight data are shown in Table 2. The polydispersity was typically 2.7. The diameters of the polymer particles were measured by dynamic light scattering (model Zeta Plus, Brookhaven Instrument) and from pictures taken by an optical microscope (Olympus AH-2). Magnification for the optical microscopy was 150−375 times. Other experimental details are described in our previous work.[9]

III. Results and Discussion

Solubility of Surfactants in CO_2 and Water. Because the hydrophilic surfactant was added to the polymerization reaction in supercritical carbon dioxide, it must be soluble in CO_2 and CO_2/monomer mixtures as well as in water. Surfactants such as SAM 185, Pluronic L61, and Pluronic L62 have been chosen because they have both a relatively large fraction of hydrophilic PEO repeat units and lipophilic PBO or PPO block(s) to adsorb to PEHA. These hydrophilic surfactants are soluble in both water and CO_2, as shown in Table 1. The solubility of Pluronic L61 (0.8 wt %) was only slightly lower than that of CO_2-philic Monasil PCA (1.0 wt %) while those of Pluronic L62 and SAM 185 were much lower. However, we found that the amount of hydrophilic surfactant added in the reaction mixture could be well above the solubility limit in CO_2. The monomer acts as a cosolvent to raise the surfactant solubility. As the polymer particles grow, dissolved surfactant molecules adsorb on the surfaces of the particles. Excess insoluble surfactant diffuses into the CO_2/monomer mixture to replace the adsorbed surfactant. When the polymer particles fully grew about 6 h after the initiation, all of the surfactant (3−11% of monomer) initially added to the bottom of the reactor entirely disappeared.

The water solubility of the hydrophilic surfactants was measured by dissolving known amounts of the surfactants in water and observing the turbidity of the surfactant/water mixture. Water was added until the mixture became clear. The solubility values for the hydrophilic surfactants are shown in Table 1. SAM 185 had the largest solubility because it had the largest weight percent of PEO groups per molecule. To measure the solubility of Monasil PCA, it was dissolved in water with overnight stirring and undissolved surfactant was allowed to settle. The supernatant was added to a vial, which was then dried to determine the weight of
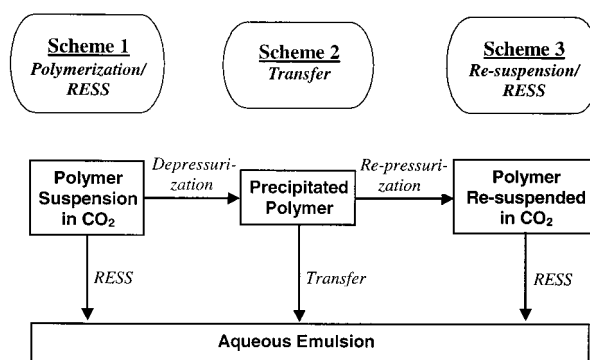

Figure 3. Processes for the preparation of polymer latexes in water.

surfactant at 343.2 K for 1 day. The solubility of Monasil PCA, 0.005 g/100 g of water, was only $1/200$ times as small as that of Pluronic L61, consistent with the small number of hydrophilic groups per molecule.

Methods for the Formation of PEHA Latexes in Water. There are three possible schemes for making a polymer latex from a liquidlike polymer as shown in Figure 3. In the new polymerization/RESS method, a polymer suspension obtained from polymerization with CO_2-philic and hydrophilic surfactants is expanded rapidly into water. In the transfer method, the bulk polymer is placed into water while the mixture is agitated. The bulk polymer may be prepared either by the conventional polymerization or by supercritical fluid polymerization. The resuspension/RESS method is almost the same as the polymerization/RESS method. The only difference is that the polymer suspension is obtained by repressurizing and resuspending the depressurized polymer suspension. In a companion study,[25] we add hydrophilic surfactants to water directly to stabilize emulsions.

Polymerization/RESS Method. Polymer suspensions obtained by polymerization of 2-EHA with a CO_2-philic surfactant and a hydrophilic surfactant were expanded rapidly through a capillary tube into water to make a stable emulsion. Advantages of this technique include the following: (1) only small amounts of hydrophilic surfactant are needed and (2) this suspension may be sprayed into pure water, which does not contain any surfactant. One disadvantage is that the hydrophilic surfactant must have some solubility in CO_2. The emulsion was stable for up to 15.6% polymer content.

The fluid velocity at the end of the nozzle is an important factor in the rapid expansion of supercritical solutions. At velocities of less than 20 m/s, the aqueous
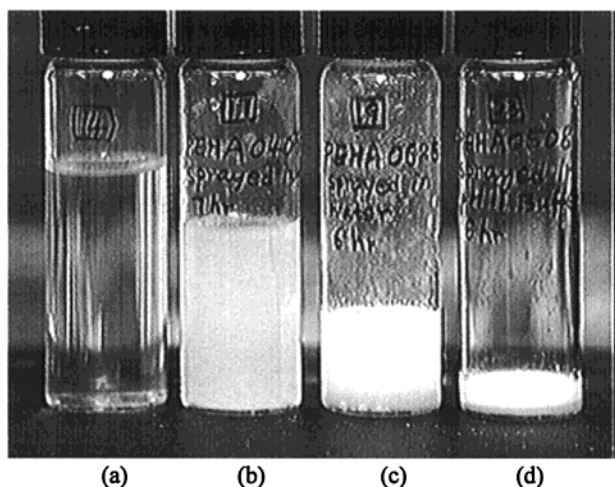
Figure 4. Stability of PEHA particles prepared by polymerization/ RESS as a function of surfactant and pH: (a) 11% Pluronic L61, pH 11 buffer solution, (b) 5.3% Monasil PCA and 3.8% Pluronic L61, pure water; (c) 5.0% Monasil PCA and 5.3% Pluronic L62, pure water; (d) 5.0% Monasil PCA and 5.2% SAM 185, pH 11 buffer solution.

polymer emulsion was not formed. However, it was formed at higher velocities (>40 m/s), preferably in the range of 70−110 m/s. Because we do not know the exact condition of the fluid at the end of the nozzle, the above velocities were estimated from the CO_2 flow rate at the syringe pump and the cross-sectional area of a 100 μm capillary tube, assuming atmospheric pressure and room temperature.

(a) Emulsions Obtained by the RESS/Emulsification Method. Aqueous emulsions were obtained by expanding the PEHA suspension synthesized in supercritical CO_2 with a CO_2-philic surfactant and a hydrophilic surfactant into water or basic buffer solutions (Table 2). For polymers (with MW 110 000−120 000) prepared with any of the hydrophilic surfactants, the emulsification was quite successful. The visual quality of the resulting emulsions was good or very good, except for one with Monasil PCA and Pluronic L61. After expansion, the emulsion with Pluronic L61 contained visible particles in the aqueous phase and on the wall. This limitation in the emulsion quality results from the low hydrophilicity of Pluronic L61. The polymer content in the emulsion is directly related to the duration of the spray. Therefore, a small polymer content for the first two samples does not necessarily mean that Pluronic L61 is not good for emulsion stabilization. In Table 2, the average particle size of the emulsions ranges from 1.2 to 2.7 μm, except for the first sample. For control experiments, PEHA was synthesized with three different combinations of surfactants: (1) no surfactant, (2) only a hydrophilic surfactant, and (3) only a CO_2-philic surfactant. In all cases the amounts of the reaction medium (CO_2), the initiator, and the surfactant were 20, 0.04, and 0.2 g, respectively. The amount of monomer was 4 g for the polymer without any surfactant and 2 g for polymers with a hydrophilic surfactant or a CO_2-philic surfactant. The molecular weights of polymers were almost the same as those in Table 2, except for the experiment with Pluronic L61.

Figure 4 shows the conditions where the PEHA particles are stable in water. The polymer particles synthesized with the 11% Pluronic L61 surfactant and sprayed into an aqueous solution were not stable at all in the pH 11 buffer solution or in pure water. Though

the particles were initially dispersed, all of the polymer particles aggregated and floated on the surface in a few minutes (Figure 4a). Polymers synthesized without any surfactant or with only Monasil PCA did not disperse or only slightly dispersed in water (not shown in the figure). When they were expanded into a basic solution or a basic buffer solution, the polymer drops were dispersed at first but were aggregated and floated on the surface as oily drops or chunks in a few minutes. These polymer drops could not be redispersed with vigorous agitation or even with sonication. Monasil PCA by itself does not stabilize the aqueous emulsions because not enough carboxylate groups are present to disperse the polymer particles in water. However, when the polymer was synthesized with two surfactants, Monasil PCA (CO_2-philic surfactant) and Pluronic L61 or L62 (hydrophilic surfactant), it formed a stable emulsion in water (Figure 4b,c). Some of the polymer particles, however, adhered to the vial wall after a week. For SAM 185, a very stable emulsion was produced in pH 8 or 11 buffer solutions and the particles did not adhere to the wall (Figure 4d).

Figure 5 shows that the polydispersity is large for two aqueous emulsions formed by RESS into pure water and the pH 11 buffer solution. The particles emulsified in pure water (approximately 2−3 μm average diameter) were larger than those in the pH 11 buffer solution. When the supercritical CO_2/polymer suspension was sprayed, CO_2 dissolved into water, forming carbonic acid (H_2CO_3) and thus lowering the pH values to 3−4. When the solution was exposed to air, carbon dioxide evaporated. The pH recovered to the original pH of water in 60 h (Table 3). When the polymer suspension was expanded into buffer solutions, however, the carbonic acid reacted rapidly with sodium phosphate, maintaining the pH value near neutral at 6.5−7. The carboxylic group, −COOH, in the Monasil PCA surfactant was deprotonated to form −COO$^-$ in the basic solution, preventing the polymer particles from adhering to the glass wall as discussed later. The blurred images in the background of Figure 5 appeared because the exposure time for the camera had to be set to about 5−10 s for the best quality pictures. Emulsion samples for microscopy were prepared by placing 1 drop of an emulsion sample onto a glass slide, which was covered by another glass slide.

Figure 6 shows the sizes of the particles in the pH 11 buffer solution formed by rapid expansion of the PEHA suspension stabilized with Monasil PCA and SAM 185. The size distribution of polymer particles ranged widely from 20 μm to below 1 μm. The average size was around 2−3 μm (2.4 μm average by light scattering) in diameter, while the concentration of the polymer was 4.5%. The diameters of very large particles might have been somewhat overestimated as they were flattened to form ellipsoids between the two glass slides because of the surface tension of water and the weight of the upper glass slide. For example, if the gap between the two slides is 5 μm and the diameters of large ellipsoidal particles are 10 and 20 μm, the actual sizes of the particles before they were flattened were 8 and 13 μm, respectively. In Figures 5 and 6, the emulsion stabilization was similar for SAM 185 and Pluronic L62 surfactants. Polymer particles were a little bit more stable in water for Pluronic L62 than for Pluronic L61 as expected from its greater hydrophilicity, as reflected in its higher EO fraction and greater water solubility.
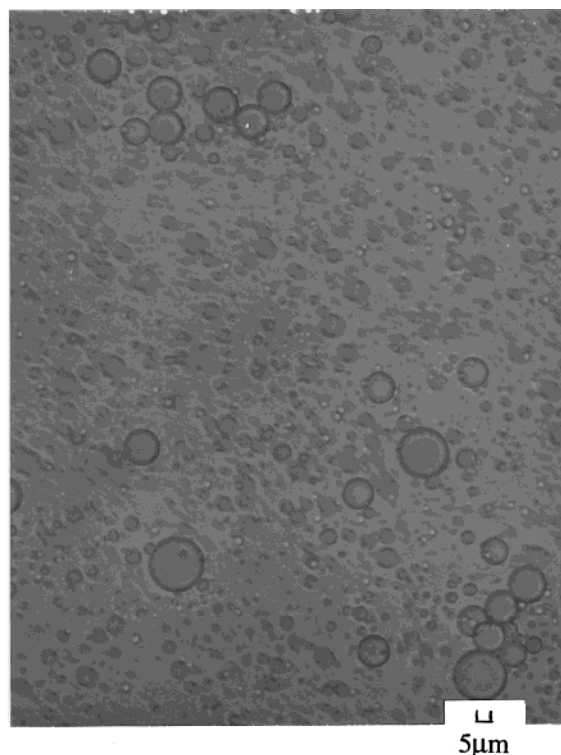
(a)
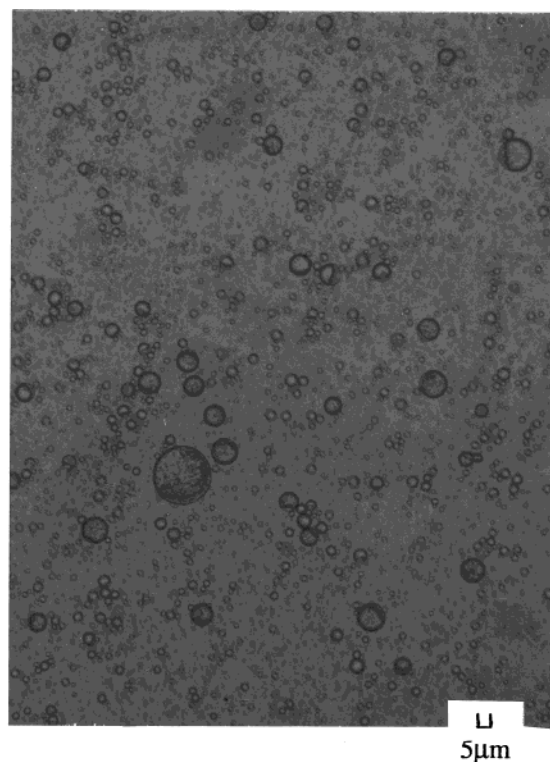
(b)

Figure 5. Particles in PEHA emulsions formed by RESS of polymer suspensions stabilized with 5% Monasil PCA and 5% Pluronic L62 into (a) pure water and (b) a pH 11 buffer solution.

Table 3. Variation of the pH Values of Aqueous PEHA Emulsions with Time after Spraying the Supercritical Fluid Polymer Suspension into Pure Water and Buffer Solutions

aqueous medium	before spray	just after spray	after 12 h	after 60 h
water	6.7	3.7	3.9	6.8
pH 8 buffer	8.0	6.5	6.6	
pH 11 buffer	11.0	6.8	7.0	

(b) Effect of Sonication on the Particle Size. When the PEHA polymer suspension formed with hydrophilic SAM 185 together with CO_2-philic Monasil PCA was expanded through a nozzle into water, small polymer particles of around $1-2$ μm were formed. When the latex was very concentrated, the particles started to agglomerate. In a few weeks, the agglomerates grew to $20-50$ μm (Figure 7) and a dense polymer layer was formed at the top of the vial. Some of the particles even grew to 1000 μm. The particles adhered to the wall when they were dispersed in pure water. This type of agglomeration was not common for particles covered with other surfactants (Pluronic L61 and 62).

By strong sonication, however, the agglomerated particles were easily dispersed to form very small and uniform particles within 5 min (Figure 8). The sonicated polymer latexes were much more stable and settled 60 times slower than the original ones. The emulsions of other polymers were also sonicated to make stable latexes, which had an average particle size of about 0.3 μm. Figure 9 shows that, after 5 days, all of the sonicated emulsions were extremely stable in both water and pH 11 buffer solution for polymers stabilized with Monasil PCA and Pluronic L62 (or SAM 185). Even after 18 days, they started to settle only slightly.
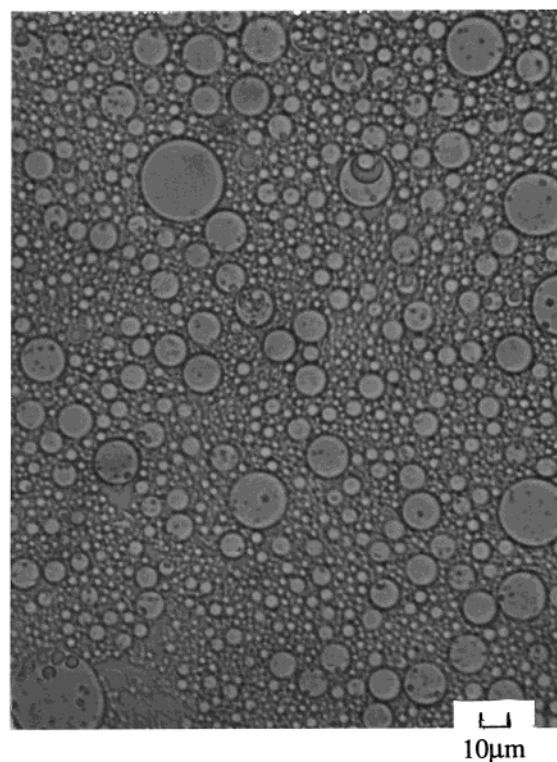

Figure 6. Particles in the pH 11 buffer solution formed by RESS of PEHA suspensions stabilized with Monasil PCA and SAM 185 surfactants. The polymer content is 4.5%.

We defined the sedimentation time as the time required for half of the emulsion to become clear or only slightly turbid. These emulsions were sonicated 16 days after they were first formed. The sedimentation times ranged from 70 to 140 days (Tables 2 and 4). The
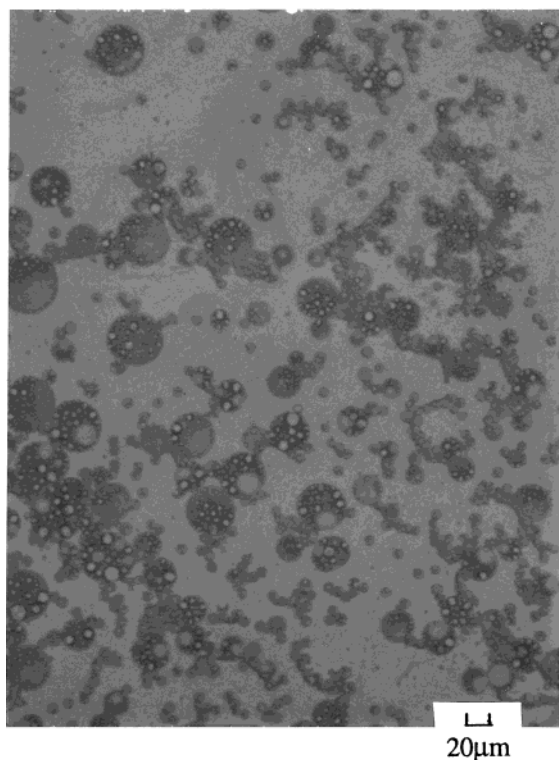
Figure 7. Concentrated PEHA (15.6%) forms large particles by agglomeration of small particles in 2 weeks after RESS. The polymer was stabilized with Monasil PCA and SAM 185 surfactants and was then expanded into pure water.
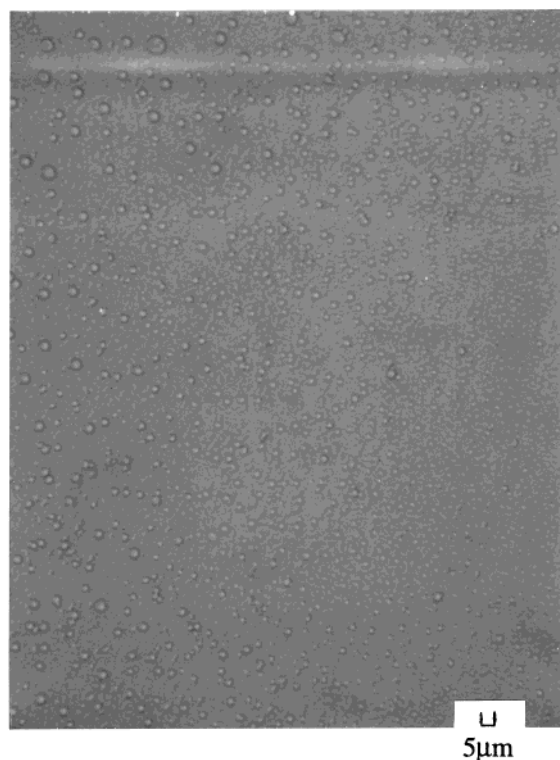

Figure 8. Size reduction of PEHA agglomerates by ultrasonic vibration into very small particles. The polymer was stabilized with 5% Monasil PCA and 5% SAM 185 surfactants and was expanded into water.

$$t = 9\eta h/2\Delta\rho g r^2$$

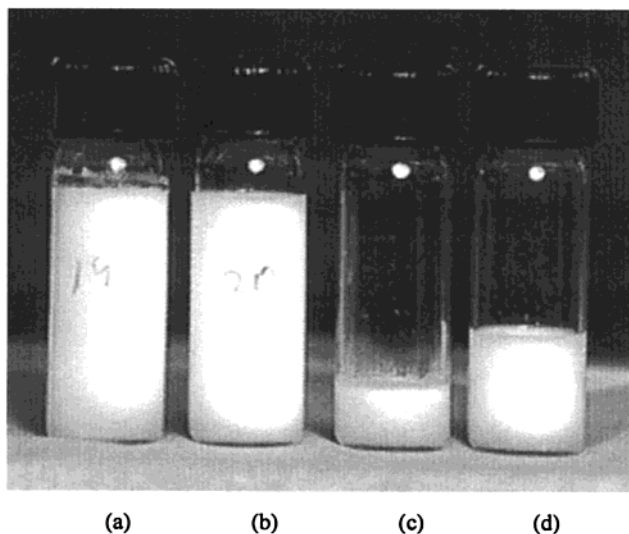sedimentation time may be calculated with Stokes' law, $t = 9\eta h/2\Delta\rho g r^2$, where t is the sedimentation time, η is

Figure 9. Stability of the sonicated PEHA latexes formed by RESS of a polymer suspension stabilized in CO_2 with Monasil PCA and a hydrophilic surfactant. Hydrophilic surfactants and aqueous media are (a) Pluronic L62 and water, (b) Pluronic L62 and a pH 11 buffer solution, (c) SAM 185 and water, and (d) SAM 185 and pH 11 buffer solution, respectively. The picture was taken 5 days after sonication.

the continuous-phase viscosity, h is the sedimentation distance, $\Delta\rho$ is the density difference between the dispersed and continuous phases, and r is the droplet radius. For a particle with a diameter of 0.3 μm, the calculated sedimentation time was 81 days for a sedimentation distance of 1.55 cm. Therefore, the estimated sedimentation time was close to the calculated one.

(c) Effect of Basicity on the Emulsion Stability. When the polymer suspension was expanded rapidly into pure water, some of the polymer particles adhered to the wall in a few days (Tables 2 and 4). As stated above, the solution is initially acidic and becomes neutral after the CO_2 evaporates. In pure or acidic water, hydrogen bonds may be formed between the oxygen atoms (as $-Si-O-Si-$) on the glass surface and the acidic hydrogen in Monasil PCA. The hydrogen atoms in the silanol groups may also form hydrogen bonds with the oxygen atoms of Monasil PCA. Furthermore, the ether oxygen atoms in PEO, PPO, and PBO of the hydrophilic surfactants and the silanol groups on the glass surface form hydrogen bonds. Malmsten et al.[26] showed that PEO adsorbs on silica in neutral water. The interactions with the surfactants and glass surface led to the observed particle adhesion.

When expanded into the buffer solution, the aqueous polymer emulsions were stable and did not adhere to the wall (Tables 2 and 4). High basicities may prevent the agglomeration of the polymer particles by producing negative surface charges on the Monasil PCA for electrostatic stabilization. Therefore, latexes formed in the buffer solution were more stable and lasted longer than those in pure water. High basicities also prevent the polymer particles from adhering to the wall. In the basic solution, the glass surface becomes negatively charged as the silanol groups on the surface are deprotonated, and these charges repel the carboxylate anions of Monasil PCA. Above the critical desorption pH of 10.4–10.8, PEO loses its affinity for the surface because of the negative surface charge.[26] Thus, the latex particles covered with the hydrophilic polymers as well as Monasil PCA did not adhere to the glass wall at high

Table 4. Dispersions of PEHA Formed in Either Water or Buffer Solution by Expanding through a Nozzle

| | surfactant in CO_2 | | | | | | | |
method	CO_2-philic (g/100 g of monomer)	hydrophilic (g/100 g of monomer)	polymer MW (kg/mol)	liquid medium	polymer content in water (g/100 g)	visual quality[a] after shaking	particle size, original (μm)	particle size after sonication (μm)
redispersion	Monasil (5.0)	Pluronic L62 (5.3)	103	water	0.17	good	1.1	0.30
	Monasil (5.0)	SAM 185 (5.0)	88	buffer at pH 11	2.8	very good	0.44	0.32
transfer	Monasil (5.0)	Pluronic L62[b] (5.3)	113	water	1.0	little dispersed	N/A	N/A
	Monasil (5.0)	Pluronic L62[b] (5.3)	113	buffer at pH 11	1.0	agglomerated	N/A	N/A

[a] Categories for visual observations of the latexes are given in Table 2. [b] Pluronic L61 with or without Monasil PCA shows similar results.

pH. When these latexes in the buffer solution were sonicated, the suspensions were stabilized for more than 3 months.

Transfer Method. We tried to make latexes directly from PEHA bulk polymer. The PEHA suspension was synthesized with Monasil PCA surfactant and Pluronic L62 (or SAM 185), in the presence of supercritical CO_2 at 345 MPa and 373.2 K. The polymer was then depressurized to the atmospheric pressure and cooled to room temperature, forming a bulk polymer. To make an emulsion directly from the polymer, the polymer was then transferred into a vial containing pure water and a basic solution with agitation with a magnetic stir bar. Rigorous stirring or shaking did not produce a stable latex. The polymer remained mostly coalesced in water (Table 4). The same behavior was observed in the basic buffer solutions. Even after intense sonication for 12 min, we could not disperse the coalesced polymer. Large polymer agglomerates or visible particles were still suspended in water. The surfactant might be trapped inside the large polymer particles such that external forces cannot overcome the van der Waals force between the polymer molecules. We found in our companion study that the transfer method will work when a hydrophilic surfactant is directly present in the aqueous solution.[25]

Resuspension/RESS Method. After two-thirds of the PEHA suspension, stabilized with Monasil PCA and Pluronic L62, was expanded into an aqueous medium to make emulsions, the remaining polymer suspension became dense and the stir bar stopped spinning. When CO_2 was added to 34.5 MPa, the stir bar started rotating in about 1 h. The temperature was lowered to room temperature, and after 2 h, it was raised to 338.2 K to resuspend the polymer particles. The quality of emulsion formed by rapid expansion of this resuspended polymer was almost the same as the one obtained from the original polymer suspension, the first sample in Table 4.

Another PEHA suspension was synthesized with Monasil PCA and SAM 185 surfactants for 6 h. When the PEHA suspension was depressurized to 10 MPa and cooled to room temperature, the suspended polymer particles settled. The polymer particles then aggregated, forming a bulk polymer whose viscosity increased substantially, and the stir bar stopped spinning. The pressure was further dropped to 1.4 MPa by removing some of the CO_2. It could have been lowered even further, but we did not want to remove any polymer from the vessel. The polymer was maintained at this mild condition for about 1 h. Then CO_2 was charged again into the reactor to 34.5 MPa, and the temperature was raised to 338.2 K. In 30 min the magnetic stir bar became free and started to rotate, dispersing the bulk polymer phase into particles. The aqueous latex formed by rapid expansion of this resuspended polymer suspen-

sion was nearly as good as the one obtained without depressurization (the second sample in Table 4).

On the other hand, PEHA synthesized without any CO_2-philic surfactant was hard to resuspend in supercritical CO_2. This proves that the CO_2-philic surfactant molecules coat and remain on the surface of the particles, even after the polymer particles agglomerate. With stirring, the surfactant molecules on the surface allow the agglomerated particles to be redispersed. The procedure offers a new technique for transporting emulsions. The polymer suspension may be stored and shipped at milder conditions (296.2 K and 1.4 MPa) than the reaction condition (338.2 K and 34.5 MPa). Once it is delivered to the destination, the original condition is recovered by adding CO_2 and raising the temperature. The polymer latex may be resuspended in CO_2 and sprayed to form coatings or expanded into aqueous solutions to form a latex.

IV. Conclusions

Rapid expansion of PEHA suspensions in supercritical CO_2, containing a hydrophilic as well as a CO_2-philic surfactant, into water produces stable aqueous latexes. Aqueous emulsions with up to 15.6% polymer were stable for weeks. The aqueous latexes could also be formed by RESS after depressurization and resuspension of the polymer dispersion in CO_2. The direct transfer method was not successful in producing stable latexes. The latexes were more stable in basic buffers than in pure water because of more effective deprotonation of the anionic stabilizer. Basic buffers are especially effective in preventing polymer particles from adhering to glass surfaces. Sonication produces polymer latexes stable for up to 3 months by reducing the particle size. The synthesis of water-dispersible polymer particles in CO_2, which may be transferred to water without the need for organic solvents, offers the possibility of new environmentally benign coatings and adhesives.

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