Poly(vinyl acetate) and Poly(vinyl acetate-*co*-ethylene) Latexes via Dispersion Polymerizations in Carbon Dioxide

Dorian A. Canelas,† Douglas E. Betts, and Joseph M. DeSimone*

Department of Chemistry, CB #3290, Venable and Kenan Laboratories, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290 and Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905

Matthew Z. Yates and Keith P. Johnston*

Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712

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ABSTRACT: The preparation of stable dispersions of poly(vinyl acetate) or ethylene/vinyl acetate copolymers via dispersion polymerizations in a carbon dioxide continuous phase has been investigated. The effectiveness of stabilizers of various chemical compositions and architectures was compared. Both fluorinated and siloxane-based stabilizers including homopolymers, block copolymers, and reactive macromonomers were employed. Effects of variations in the reaction temperature, pressure, stabilizer composition, stabilizer concentration, and use of cosolvents on the resulting product were investigated. A turbidimetry technique was used successfully to monitor dispersed-phase volume fractions, particle sizes, and number densities during the polymerizations and to give the final particle sizes at the end of the polymerizations. The fluorinated stabilizers gave rise to smaller particles and more stable latexes when compared to the siloxane-based stabilizers.

Introduction

The free-radical polymerization of vinyl acetate (VAc) can be carried out in bulk, in solution, or via heterogeneous methods such as suspension, emulsion, and dispersion polymerizations. One-third of all VAc monomers are converted to polymeric latexes for use in coatings,[1] and thus the emulsion polymerization of vinyl acetate, the predominant commercial process, has been heavily studied.[2−4] Nonaqueous dispersion polymerizations of VAc in liquid alkanes such as octane, which are not used for industrial production, have also been reported in the literature.[5−10] In addition, since both VAc and ethylene have reactivity ratios equal to 1, they copolymerize in a completely statistical manner and a copolymer of any composition can be prepared.[11,12] Because of the ability to tune polymeric properties by varying the amount of ethylene incorporation, these ethylene−vinyl acetate (EVA) copolymers find use in a tremendously wide variety of applications ranging from high-impact films to high-performance paints. Because VAc and ethylene are both soluble in CO_2, dispersion polymerization constitutes the mechanism of choice in the work presented herein, which aims at the production of stable poly(vinyl acetate) (PVAc) and EVA latexes in CO_2.

Dispersion polymerizations are governed by a delicate interplay which includes the partitioning and interactions of all of the reaction mixture components,[13] and the effectiveness of the surfactant represents a key component in the preparation of a stable latex.[14] The stabilizers studied in these experiments were carefully selected, designed, and synthesized on the basis of the known solvency in CO_2 and the established criteria for steric stabilizer effectiveness. Three different types of stabilizers were studied: CO_2-soluble homopolymers, amphiphilic diblock copolymers, and copolymerizable macromonomers. While all of these general types of stabilizer architectures have been shown to be effective in a CO_2 continuous phase, their efficacy in protecting VAc-based latex particles from coagulation has not been established. First, poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) homopolymer, which is interfacially active in other systems,[15,16] was selected for study because of its extremely high solubility in CO_2.[17] Poly(dimethylsiloxane) (PDMS) homopolymer was also selected as a stabilizer because of its CO_2-philic nature; from an economic standpoint PDMS would be the ideal macromolecular stabilizer in a CO_2 system. The vinyl-terminated PDMS macromonomer was synthesized and investigated herein because it has been shown to copolymerize well with VAc,[18] and the PDMS chains should impart stabilization by chemically grafting to the surface of the particles in situ. Theoretically, block copolymers of either PDMS or PFOA with a PVAc anchoring group provide the best stabilizing systems because they have been specifically designed to be interfacially active in a PVAc/CO_2 system. These block copolymers were previously difficult to access through traditional synthetic methodologies, but recent breakthroughs[9,19,20] in controlled free-radical polymerization techniques have made the synthesis of these materials straightforward. These surfactants have been compared and contrasted in the polymerization studies presented herein.

Turbidity spectra may be analyzed by Mie scattering theory to determine particle size and dispersed-phase volume fraction. This noninvasive technique has been used to study the nucleation and growth of latex particles during emulsion polymerization of styrene and VAc in water[21] and during the dispersion polymerization of methyl methacrylate (MMA) in supercritical CO_2.[22]

* To whom correspondence should be addressed (e-mail) desimone@unc.edu; kpj@che.utexas.edu.
† Current address: Thomas Lord Research Center, Lord Corp., 405 Gregson Drive, Cary, NC 27511.

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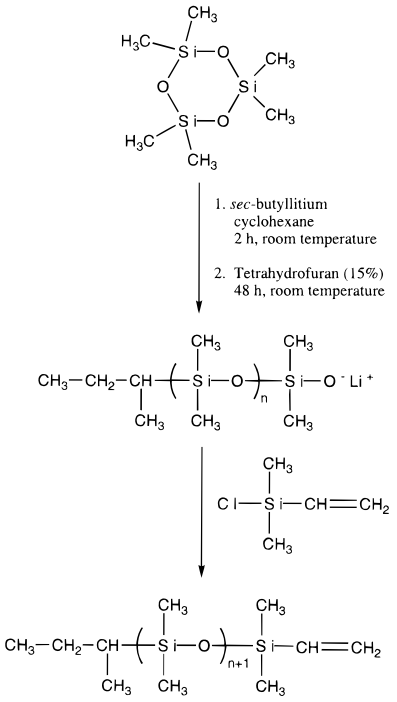
For the highly plasticized particles produced in this study, an in situ technique is particularly desirable. Since particles coalesce during depressurization, techniques such as electron microscopy provide a limited description of particle size. The objective of the current experiments is to follow particle nucleation and growth by turbidimetry in situ during the dispersion polymerization of VAc in CO_2. The effects of surfactants on the evolution of the particle size, particle number density, and volume fraction are examined in the first hour and at the end of the reaction to characterize the latex formation mechanism. The final particle sizes are compared with those of poly(methyl methacrylate) (PMMA) and polystyrene (PS) produced by dispersion polymerization in CO_2.[22−24]

Experimental Section

Materials. Vinyl acetate (Aldrich) and 1,1-dihydroperfluorooctyl acrylate (FOA, 3 M) were purified and deinhibited by passage through an alumina column and were deoxygenated by argon purge prior to use. Ethylene (polymer grade, Matheson) was used as received. Hexamethylcyclotrisiloxane (D_3, Acros) was kindly provided by Bayer and was purified via vacuum sublimation. A 35% (w/v) stock solution of D_3 monomer in cyclohexane was prepared and stored in a volumetric flask under an inert blanket of argon. Trimethylsiloxy-terminated poly(dimethylsiloxane) homopolymers (United Chemical Technologies) with viscosities of 1000 and 10 000 cSt were used as received. Poly(1,1-dihydroperfluorooctyl acrylate) homopolymer was synthesized via homogeneous free-radical polymerization in CO_2 following procedures previously described in the literature.[25] 2,2′-Azobisisobutyronitrile (AIBN, Eastman Kodak) was recrystallized twice from methanol. Diisobutyryl peroxide (Trigonox 187-C30, Akzo) was kindly provided by Air Products and used as received. *sec*-Butyllithium (1.3 M in cyclohexane, Aldrich) and diethyldithiocarbamic acid, sodium salt trihydrate (99+%, Aldrich) were used as received. Benzyl *N*,*N*-diethyldithiocarbamate (BDC)[9,26] and 1-(dimethylchlorosilyl)-2-(*p*,*m*-chloromethylphenyl)ethane[27] were synthesized according to previously published methods. Cyclohexane (Fisher) was stirred over concentrated sulfuric acid for ∼2 weeks, decanted, and distilled over sodium under an argon atmosphere prior to use. Tetrahydrofuran (THF, Fisher) was distilled from a sodium/benzophenone solution under an argon atmosphere prior to use. Heptane (EM Science), α,α,α-trifluorotoluene (TFT, Aldrich, 99+%), and 2-propanol (Fisher) were used as received. Carbon dioxide (SFC/SFE grade) was kindly provided by Air Products and was used as received.

Synthesis of Stabilizers. (1) Macromonomers. The vinyl-terminated PDMS macromonomers were synthesized using living anionic polymerization techniques (Scheme 1). In an illustrative reaction, 100 mL of the 35% D_3 monomer stock solution in cyclohexane under an inert argon atmosphere was initiated by 1.0 mL of 1.3 M *sec*-butyllithium and was allowed to stir for 2 h at room temperature. Then, 15% (v/v) of THF, a polar promoting solvent, which serves to break up the lithium aggregation and loosen the chain end ion pair, was added to the reaction mixture via glass syringe. After addition of the THF, the clear, colorless, homogeneous solution was allowed to propagate while being stirred at room temperature under argon for 48 h. To create the desired vinyl functionality on the chain end, 2 equiv

Scheme 1. Synthesis of Vinyl-Terminated PDMS Macromonomers

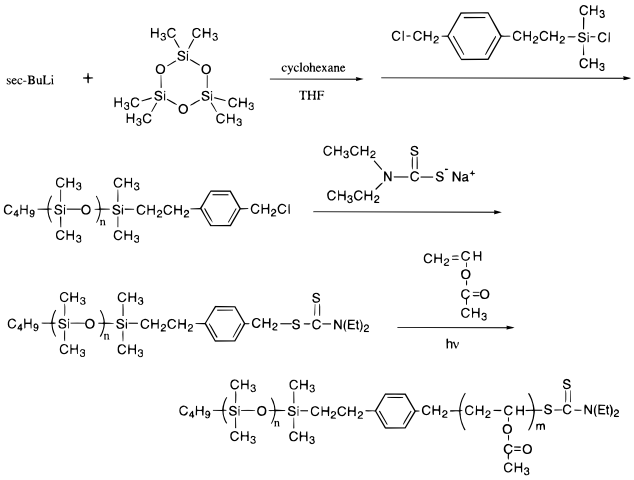


(0.387 mL) of chlorodimethylvinylsilane was added to the reaction vessel to terminate the living siloxanolate. Upon addition of the terminating agent, the clear, colorless solution became cloudy because of LiCl precipitation. The reaction solution was then filtered, and the polymer was precipitated by adding the filtrate dropwise to methanol. The viscous, clear, colorless macromonomer was then collected using a separatory funnel and dried in vacuo.

The number-average molecular weight (M_n) and polydispersity index (PDI) of the molecular weight distribution were determined by GPC in CH_2Cl_2. The vinyl-terminated PDMS macromonomer, which was employed as the stabilizer in the dispersion polymerizations, had $M_n = 3.7 \times 10^4$, PDI = 1.05, and functionality 100%. The degree of chain end functionalization was determined by ^{1}H NMR using ∼20% polymer solution in $CDCl_3$: $\delta = 0$ (multiplet, 6H, methyl groups attached to silicones), 0.5 (sextet, 1H, methine [C2] from *sec*-butyl chain end), 0.9 (triplet, 3H, methyl [C4] from *sec*-butyl chain end), 1.5 (multiplet, 5H, methylene [C3] and methyl [C1] from *sec*-butyl chain end), 5.6−6.2 (multiplet, 3H, vinyl group), 7.24 (singlet, reference solvent $CHCl_3$ peak).

(2) Block Copolymers. Poly(dimethylsiloxane-*b*-vinyl acetate) (PVAc-*b*-PDMS) diblock copolymer was synthesized via a two-step process which combined anionic and controlled free-radical polymerization techniques (Scheme 2). In the first step, anionic ring-opening polymerization of D_3 using *sec*-butyllithium as the initiator and 1-(dimethylchlorosilyl)-2-(*p*,*m* chloromethylphenyl)ethane as the terminating agent afforded PDMS with the desired chain-end functionality. The PDMS block was then converted to a controlled free-radical macroiniferter by transforming the chloro end group to diethyldithiocarbamate using the diethyldithiocarbamic acid sodium salt.[20] In the second step, the PDMS macroiniferter was used to initiate polymerization of VAc by photolysis with UV light (350 nm). At

Scheme 2. Synthesis of Diblock Copolymer: Poly(dimethylsiloxane-*b*-vinyl acetate)



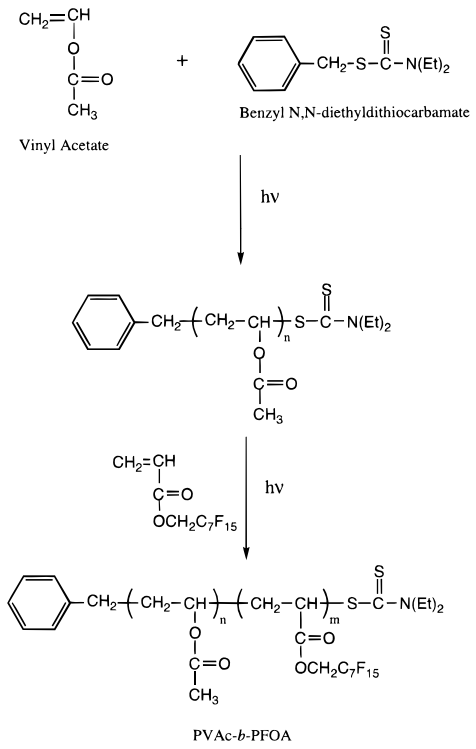
the end of the reaction, the block copolymer was precipitated into methanol, collected, and dried at room temperature in vacuo.

The molecular weight and polydispersity of the PDMS oligomer was determined prior to the addition of the second monomer using GPC (M_n of the PDMS block 2.68×10^4, PDI = 1.1). After the formation of the PVAc segment, the total molecular weight of the block copolymer was determined using GPC (M_n of the block copolymer 3.98×10^4, PDI = 1.4). The molecular weight of the PVAc block was determined by subtracting the molecular weight of the PDMS block from the total block copolymer molecular weight (M_n of the PVAc block 1.30×10^4).

Poly(vinyl acetate-*b*-1,1-dihydroperfluorooctyl acrylate) (PVAc-*b*-PFOA) diblock copolymers were synthesized in two steps via the iniferter technique (Scheme 3). The PVAc block was synthesized first due to its relatively facile characterization when compared to that of the CO_2-philic fluorocarbon block. The polymerizations of VAc were conducted in bulk and stopped at ~20% conversion. In a typical polymerization, 40.0 g of VAc monomer was added to a quartz flask equipped with a stir bar. BDC (1.0 g) and tetraethylthiuram disulfide (TD) (2 mg) were then added to the flask which was subsequently sealed with a septa and purged with argon. The solution was photolyzed at room temperature with stirring for 30 h in a 16-bulb Rayonet equipped with 350-nm bulbs. The product (BDC−PVAc) was collected by precipitation into *n*-heptane and dried at room temperature in vacuo. The BDC−PVAc was purified twice by dissolution in acetone and precipitation into *n*-heptane. The molar mass and polydispersity were determined by GPC with THF as the eluent.

The diblock copolymers were synthesized by the subsequent polymerization of FOA using BDC−PVAc as the macroiniferter. Polymerizations were conducted in TFT and proceeded homogeneously. In a typical experiment, 1.0 g of BDC−PVAc was dissolved in ~25 mL of TFT in a quartz flask equipped with a stir bar. FOA monomer (15−20 g) was then added, and the flask was purged with argon. After purging, the solution was photolyzed at room temperature with stirring for 30 h in a 16-bulb Rayonet equipped with 350-nm bulbs. The product was collected by precipitation into methanol and dried under in vacuo. The block copolymers were purified by Soxhlet extraction for ~2 days using methanol to remove any unreacted PVAc homopolymer. The composition and relative molecular weights of the blocks in the block copolymer were determined by ^{1}H NMR. For simplicity, these block copolymers will be referred to by listing the M_n of the PVAc segment followed by the M_n of the PFOA segment.

Scheme 3. Synthesis of Diblock Copolymer: Poly(vinyl acetate-*b*-1,1-dihydroperfluorooctyl Acrylate)



Polymerizations in Carbon Dioxide. Polymerizations were conducted in CO_2 in a 10-mL, high-pressure view cell equipped with sapphire windows which permit visual observation of the reaction mixture.[28] The reactor was charged with initiator (either AIBN or Trigonox 187-C30) and the desired amount of surfactant (except control reactions in which no surfactant was used); it was then purged with a flow of argon prior to the addition of monomers. When the Trigonox 187-C30 was employed as the initiator, the reaction vessel was cooled in an ice/water bath to prevent premature cleavage of the peroxide linkages; when AIBN was employed, the reaction vessel was at room temperature. VAc, cosolvent (if any), and/or ethylene were then added to the system under argon. An Isco model 260D automatic syringe pump was used to pressurize the reactor with CO_2 to ~70 bar, and the reaction mixture was heated to the desired temperature of either 25 or 65 °C (±0.1 °C), depending on whether liquid or supercritical conditions were desired. As the reaction vessel was warmed, the remaining CO_2 was slowly added to the system until the desired temperature and pressure were reached. Once the final conditions were obtained, the reaction was allowed to proceed with stirring for times that varied from 4 to 18 h. The stability of the latex was determined qualitatively by visual observation of the mixture at the end of the reaction time in the absence of stirring for ~5 min. At the end of the reaction, the vessel was quickly cooled in an ice/water bath. Then CO_2 was then slowly vented from the cell through a pressure let-down valve and was bubbled through

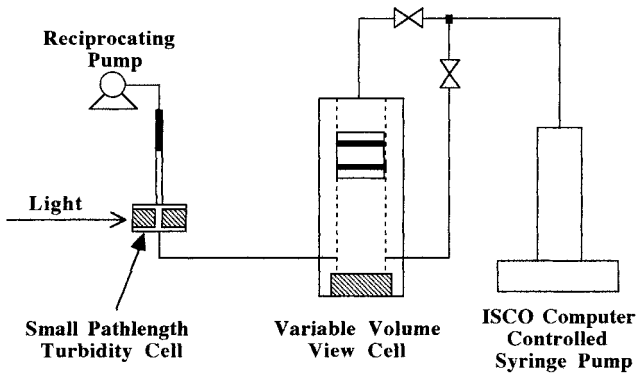


Figure 1. Schematic of turbidimetry apparatus.

n-heptane in order to collect any polymer that sprayed out during the venting process. The very small amount of polymer that was collected in the *n*-heptane during the venting process was collected by vacuum filtration over a Hirsch funnel. The remaining polymer product was removed from the reaction vessel and dried in vacuo at room temperature overnight. The yield of the dry polymer was determined gravimetrically.

Turbidity Measurements. Turbidity spectra were taken in situ during the first 2 h of selected polymerizations in supercritical CO_2 using a specially designed high-pressure turbidimetry apparatus, shown in Figure 1. The apparatus consisted of a variable-volume view cell, small path length optical cell, reciprocating mini syringe pump, and a computer controlled syringe pump (Isco model 100DX). The optical cell was a modified $^1/_4$-in. Swagelok union with quartz windows and a path length of 0.29 mm. The apparatus has been described in detail in a previous study.[22] Spectra were obtained with a Beckman DU-40 spectrometer.

To parallel the other polymerization studies, all reactions were conducted at 65 °C and 345 bar. The concentrations of the components in the reactor were kept constant at approximately 17.1 wt % VAc, 0.86 wt % surfactant, and 0.34 wt % AIBN. First, the AIBN and surfactant were loaded into the front of the variable-volume view cell, and the apparatus was purged with CO_2 vapor for ~15 min to remove oxygen. VAc (previously purged with nitrogen for 15 min) was injected into the view cell and the apparatus was sealed. A measured amount of liquid CO_2 was then added to the view cell from the Isco syringe pump. The apparatus was then pressurized to 345 bar as the view cell was submerged in a water bath preheated to 65 °C. The reciprocating pump was then started at a rate of 1 stroke/25 s.

The reaction mixtures were initially transparent at 345 bar and 65 °C, and the baseline spectra were taken immediately after the cell reached the desired temperature and pressure. After a short induction time (<5 min), the contents of the reactor became slightly turbid due to the nucleation of latex particles. The starting point of the reaction was defined as the onset of visual turbidity in the view cell. Spectra in the wavelength range of 560−760 nm were taken approximately every 5 min during the first 2 h of each reaction and at the end of the total reaction time for certain reactions.

PVAc Swelling by Compressed CO_2. PVAc has been shown to be more soluble in CO_2 than other polymers produced by dispersion polymerization such as PS and PMMA.[29] Therefore, the PVAc particles were highly swollen by CO_2 at the reaction conditions. The swelling of PVAc homopolymer sample by CO_2 was measured using a small 1-mL graduated cylinder containing a PVAc sample placed in a high-pressure view cell. The contents of the cell were brought to 345 bar and 65 °C, and the sample was allowed to swell for 12 h. At these conditions, the volume of the swollen PVAc was recorded to within ±0.05 mL by observing the meniscus. The measured swelling of PVAc by CO_2 was found to be 40 ± 10% at 65 °C and 345 bar. It should be noted that the presence of a large amount of monomer at the beginning of the reaction further swelled the particles. Also, the lower molecular weight oligomers present at the beginning of the reaction will be swollen more than the final product.

Characterization. The molecular weights and molecular weight distributions of the polymer samples were determined using a Waters 150-CV GPC with Ultrastyragel columns of 100-, 500-, 10^3-, and 10^4-Å porosities using THF as the eluent and PS standards (Showa Denko). Since PDMS is isorefractive with THF, the molecular weights and molecular weight distributions of the PDMS-based materials were determined using methylene chloride as the mobile phase, PS standards, and a modular Waters 600E GPC with three Ultrastyragel columns of linear, 10^3- and 10^4-Å porosities with a 410 differential refractometer. The morphology of the polymers was investigated using a JEOL 6400 FE scanning electron microscope (SEM). ^{1}H NMR spectra were obtained from a Bruker WM250 spectrometer.

Results and Discussion

Comparison of Stabilizers. Preliminary scouting experiments were conducted in supercritical CO_2 with AIBN initiation to investigate the effectiveness of various stabilizer compositions and architectures in the dispersion polymerization of VAc (Table 1). Initial experiments (entries 1−6) were run for a 4-h reaction time, and at these conditions, an unstabilized precipitation polymerization gave a yield of ~50%. It was hoped that the gel (Trommsdorf) effect, which is commonly observed inside dispersion polymerization latex particles, would allow the stabilized reactions to reach quantitative yields in the 4-h reaction time. However, a gel effect was not observed in these systems, and the 4-h dispersion polymerizations did not show significant increases in yields or molecular weights. Walbridge pointed out that low-T_g polymers such as PVAc and poly(ethyl acrylate) have a much less pronounced rate acceleration during dispersion polymerization when compared to polymers such as PMMA because of relatively low intraparticle viscosities.[30] In addition, because of the relatively high solubility of PVAc in CO_2[29] in comparison to the other dispersed phases that have been studied, the PVAc particles are highly swollen with CO_2 and the dramatic plasticizing effect of the CO_2 enhances the diffusion of the polymeric radical chain ends and prohibits the gel effect. A positive result from these studies was that all of the stabilizers except the PDMS homopolymer were effective in preventing the coagulation of the PVAc colloidal particles so that stable latexes were obtained.

Encouraged by this success, the next set of reactions (entries 7−13) was allowed to proceed for 18 h, and the desired high conversions were obtained. This work parallels that found in the literature,[6,7,10] where reaction times of 18−50 h are needed to achieve high conversion of VAc by dispersion polymerization. As shown in Table

Table 1. Comparison of Stabilizers for the Polymerization of VAc in Supercritical CO_2[a]

entry	stabilizer	stab wt (g)	time (h)	yield[b] (%)	M_n[c]	PDI[c]	comments
1	none	0	4	51	55	2.8	product settles
2	PDMS homopolymer[e]	0.1	4	71	31	3.5	product settles
3	PFOA homopolymer	0.1	4	47	36	2.3	stable latex
4	vinyl-terminated PDMS	0.1	4	65	27	3.8	stable latex
5	PVAc-*b*-PDMS	0.1	4	54	37	2.3	stable latex
6	PVAc-*b*-PFOA[g]	0.1	4	51	67	2.6	stable latex
7	none	0	18	78	24	2.4	product settles
8	PDMS homopolymer[e]	0.1	18	94	25	4.4	collapsed latex
9	PDMS homopolymer[f]	0.1	18	92	20	4.5	collapsed latex
10	PFOA homopolymer	0.1	18	86	34	3.5	stable latex
11	vinyl-terminated PDMS	0.1	18	92	20	6.4	collapsed latex
12	PVAc-*b*-PDMS	0.1	18	92	24	2.4	collapsed latex
13	PVAc-*b*-PFOA[g]	0.1	18	86	29	2.5	stable latex

[a] Reaction conditions: 2.0 g of VAc, 2.4×10^{-2} M AIBN; $P = 352$ (±9) bar; $T = 65.0$ (±0.1) °C. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n). [e] Viscosity, 1000 cSt. [f] Viscosity, 10 000 cSt. [g] M_n PVAc block, 1.0×10^4; M_n PFOA block, 4.3×10^4.

Table 2. Effect of Anchor-Soluble Balance (ASB) of the PVAc-*b*-PFOA Stabilizer on the Dispersion Polymerization of VAc[a]

stabilizer, PVAc-*b*-PFOA (M_n PVAc/M_n PFOA)	wt stab (g)	yield[b] (%)	M_n[c] (10^{-3})	PDI[d]
4K/43K	0.2	91	70	3.3
10K/43K	0.2	90	51	4.3
31K/20K	0.2	96	47	3.5
31K/54K	0.2	93	63	3.3

[a] Conditions: pressure, 354 (±8) bar; temperature, 65 (±0.1) °C; 18-h reaction time; 0.2 g of stabilizer; 2.0 g of VAc monomer. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n).

1, the reactions that contained PFOA-based stabilizers (either homopolymer or diblock copolymer) were stable at high conversion even in the absence of stirring. The inability of the PDMS-based stabilizers to produce stable latexes at high conversion is not surprising when the aggregation behavior of PDMS in pure CO_2 (which has been observed by SANS)[31] is considered. At lower conversions, the VAc monomer serves as a cosolvent[32] for the PDMS chains and allows them to extend into the continuous phase. However, as the VAc concentration decreases during polymerization, the dielectric constant of the solution becomes lower and the PDMS chains begin to collapse; at this point the on-set of flocculation and coagulation of the particles is imminent.

The anchor-soluble balance (ASB) of the stabilizing moiety is known to be a critical variable for the preparation of stable polymer colloids. An investigation of the effect of stabilizer ASB on the polymerization of VAc in CO_2 was undertaken using the PVAc-*b*-PFOA diblock copolymers as the stabilizers (Table 2). In all cases, the reactions proceeded to high conversion and visual observation revealed that the reaction mixtures were white, opaque, stable latexes even after cooling to 0 °C in the absence of stirring. For the range of stabilizer compositions studied, no sufficient trend in results could be identified.

Characterization of the PVAc latex in situ is particularly desirable as solid latex particles could not be collected for analysis by electron microscopy. Even when freezing the PVAc latex by cooling to −62 °C and allowing CO_2 to sublime, coalescence of the recovered latex particles was widespread. A large amount of CO_2 had dissolved in the particles on the basis of their foamy appearance. No primary particles were discernible by electron microscopy. To shed further insight on the progress of these VAc polymerizations, in situ turbidimetry measurements on this system were employed. Turbidimetry was chosen due to its success in characterizing PMMA latexes in supercritical CO_2, in that the results agreed with particle sizes determined ex situ by SEM.[22] Turbidity, τ, is defined by eq 1 as where L is

$$\tau = (1/L) \ln(I_o/I) \tag{1}$$

the path length (in cm), I_o is the incident light intensity, and I is the transmitted light intensity. For a monodisperse suspension of spherical particles, the turbidity is given by[21]

$$\tau = (3\phi K(\alpha,m))/2D \tag{2}$$

where ϕ is the dispersed phase volume fraction, D is the particle diameter, and K is the scattering coefficient, which is a function of two dimensionless parameters: $m = n_p/n_m$ and $\alpha = (\pi D)/(\lambda_m)$. In this case, λ_m is the wavelength of light in the continuous phase, n_p is the refractive index of the particle, and n_m is the refractive index of the surrounding medium. From eq 2, the ratio of turbidities at two different wavelengths for a monodisperse suspension of spheres is given by eq 3. The

$$\tau_1/\tau_2 = K_1/K_2 \tag{3}$$

particle diameter is determined with eq 3 by using an iterative procedure until the calculated ratio of scattering coefficients equals the measured ratio of turbidities. This turbidity ratio method has the advantage that it is not necessary to know the dispersed-phase volume fraction for particle size determination. However, this technique is limited to regimes where the scattering coefficient varies significantly with particle diameter.[21]

If a polydisperse latex is treated as monodisperse, an "apparent" average size will be obtained from eq 3 that is weighted by larger sized particles. The type of average obtained (i.e., weight average, volume/surface average, etc.) is not well defined and may vary significantly with the choice of wavelength of light.[33] Because of uncertainty in the refractive index of the dispersed phase in our systems, we were not able to measure polydispersities. The latex will be treated as monodisperse, and the diameters obtained will be reported as average diameters. The objective was to evaluate semiquantitatively the performance of a variety of

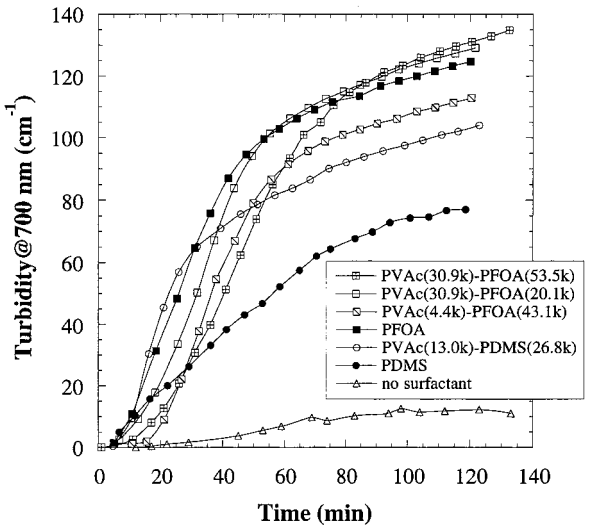


Figure 2. Turbidity at 700-nm wavelength versus time for various surfactants.

surfactants used in dispersion polymerization based upon average particle sizes.

The turbidity for each reaction at a temperature of 65 °C, a pressure of 345 bar, and a wavelength of 700 nm is plotted versus time in Figure 2. The reactions stabilized with the PFOA-based surfactants were the most turbid after 1 h. The turbidity of the reaction stabilized with PVAc-*b*-PDMS increased the most rapidly for the first 30 min, but then the slope became smaller than those with the PFOA-based block copolymers. The PDMS homopolymer produced much smaller turbidities and was also the only surfactant that was unable to stabilize all of the latex produced during the first 2 h of the reaction. After 20 min, a few small PVAc droplets could be observed on the front window of the view cell. At 40 min, a bulk PVAc-rich phase was observed which had precipitated to the bottom of the reactor and continued to grow in size during the reaction. In contrast, the reaction conducted without surfactant exhibited very low turbidities as the polymer precipitated during the reaction. A bulk PVAc-rich phase was visible at the bottom of the cell after ~40 min.

To further investigate latex formation and stabilization as a function of surfactant architecture and ASB, particle size measurements were conducted using the turbidity ratio method. The refractive indices of the particle phase and continuous phase, which were both mixtures, had to be estimated in order to calculate final particle size. The refractive index of pure CO_2 is ~1.19 at the temperature and pressure used in this study.[34] The refractive indices of PVAc and VAc are 1.45 and 1.40, respectively.[32] Given the pure component refractive indices, the refractive index of a mixture can be estimated.[35] However, the ternary phase behavior of CO_2/VAc/PVAc mixtures is unknown.

For the estimation of refractive indices during the first hour of the reaction, it was assumed that the partition coefficients of the monomer and CO_2 are the same. The molar volume of CO_2 dissolved into the polymer phase was estimated to be 44 cm^3/mol,[36] and its refractive index was assumed to be equal to that of pure CO_2 at this molar volume.[34] The refractive index of the VAc was assumed to be 1.40 in both the continuous phase and particle phase. The Lorenz−Lorentz mixing rule[35] was used to estimate the particle-phase and continuous-phase refractive indices. The solubility of PVAc in the continuous phase was assumed to be zero, and ideal mixing was assumed for the continuous phase. To estimate the error in the particle refractive index, it was assumed that the swelling of the particle phase was in the range of 100 ± 50%. For 100% swelling (50% PVAc, 43% CO_2, 7% VAc), the dispersed phase refractive index was estimated to be 1.36. For a monomer concentration of 17 wt %, the continuous-phase refractive index is estimated to be 1.24. The uncertainty in swelling leads to an uncertainty in the refractive index ratio (n_p/n_m) of 1.10 ± 0.02. The effect of changing composition during the reaction was neglected.

The scattering coefficients were calculated by using a published subroutine.[37] The average particle diameter was then calculated from the turbidity at 560 and 700 nm by using a refractive index ratio of 1.10. The particle sizes were recalculated by using refractive index ratios of 1.12 and 1.08 to estimate the error in the particle diameters due to the uncertainty in refractive index. The uncertainty in diameter was found to be ~±20%, for all measurements. This error in particle size measurement does not affect the comparison of particle sizes obtained by different stabilizers because the refractive index ratio will be similar for all latexes. The calculated diameters were inserted into eq 2 to estimate the dispersed-phase volume fraction. The volume fraction divided by the volume of a single particle was used to estimate the particle number density. When results for different stabilizers were compared, the same relative trends in particle size, dispersed-phase volume fraction, and particle number density were observed for calculations at both the low and high extremes (1.08−1.12) of the refractive index ratio.

The above equations for turbidimetry are based upon the assumption that multiple scattering can be neglected. An aqueous PS latex standard was used to estimate the maximum optical density where multiple scattering was not present. For a 480-nm monodisperse latex, it was found that the turbidity ratio at 700 and 560 nm was not affected below optical densities of 1.3, in agreement with a previous study.[22] During the dispersion polymerizations, no size measurements were made for optical densities above 1.3.

Figure 3 shows the average particle diameter, dispersed-phase volume fraction, and particle number density, respectively, versus time for the PFOA-based stabilizers. The particle size measurements could only be conducted in the first 40 min of these reactions after which multiple scattering introduced significant error. From Figure 3a, it can be seen that the PFOA homopolymer produced the largest diameter latex particles. The diameters for the particles obtained from the experiments with PVAc-*b*-PFOA diblock copolymers as stabilizers were smaller than for those with the PFOA homopolymer as the stabilizer. The average particle diameter obtained with PVAc-*b*-PFOA (31K/54K) was significantly smaller than the values obtained with the other stabilizers.

The dispersed-phase volume fractions shown in Figure 3b were nearly within the range of experimental error for all PFOA-based stabilizers, suggesting similar reaction kinetics. This is in agreement with Table 1, which shows similar conversions for all reactions after 4 h. The particle number density shown in Figure 3c

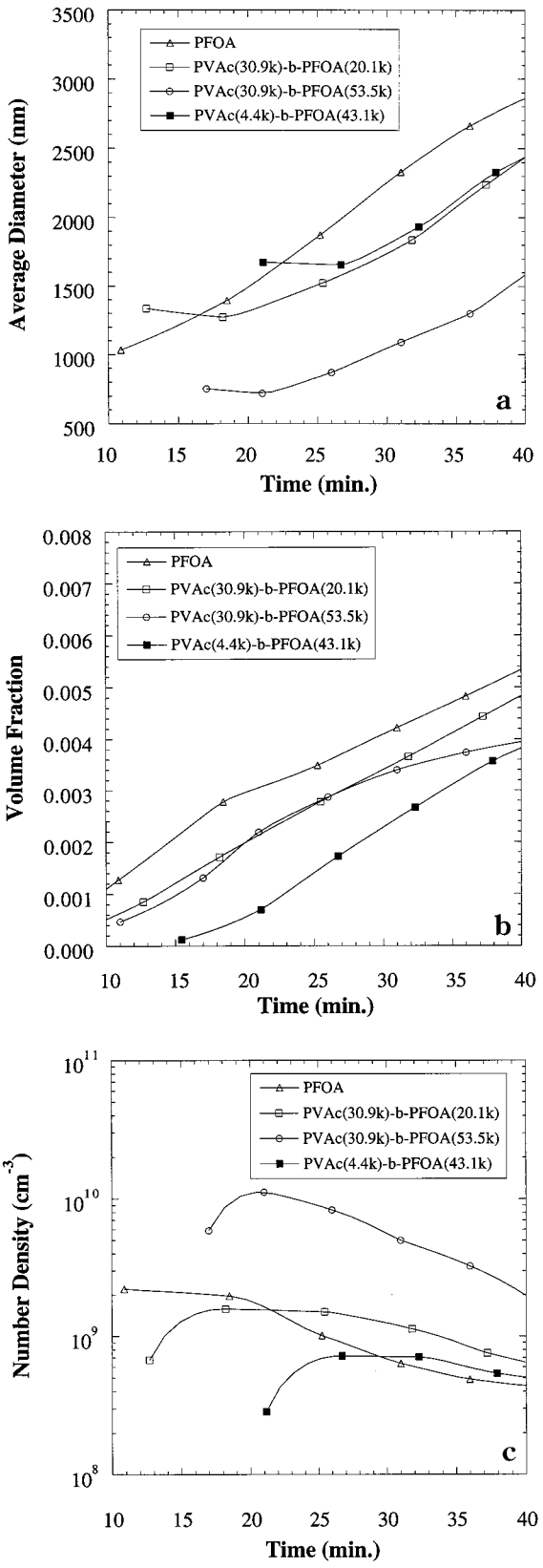


Figure 3. Dispersion polymerizations of VAc in CO_2 using PFOA-based surfactants: (a) average particle diameter, (b) dispersed-phase volume fraction, and (c) particle number density.

was highest for PVAc-*b*-PFOA (31K/54K) and lowest for PVAc-*b*-PFOA (4K/43K). The PFOA homopolymer and the PVAc-*b*-PFOA (31K/20K) diblock copolymer stabilized an intermediate number of particles. From Figure 3c it appears that the particle number density goes through a maximum value. The maximum value will be taken for comparison of the particle number stabilized by different stabilizers. The decrease in particle number density with time is most likely due to contributions from multiple scattering. Multiple scattering causes the turbidity ratio to approach 1.0 and the diameter and particle number density to approach asymptotes of ~3.3 μm and ~5.0×10^{-9} cm^{-3}, respectively.

Dawkins and Taylor showed that the final particle size obtained from a dispersion polymerization strongly depends on the molecular weight of the soluble, stabilizing segment for diblock copolymeric stabilizers.[38] Higher molecular weight stabilizing blocks produce smaller particle sizes because the longer tail lengths are capable of stabilizing more surface area. For the two copolymers with the 3.1×10^4 molecular weight anchor block (31K), the one with the higher molecular weight soluble segment (tail) (54K) produces smaller particles and stabilizes a higher number of particles than the one with the lower molecular weight tail (20K), as expected. However, the block copolymer with the 43K molecular weight tail produces almost identical particle sizes, with number densities slightly lower than for the surfactant with the 20K tail. On the basis of the volume fractions and particle number densities, it appears that the lower molecular weights of the anchoring segments on the block copolymeric stabilizers with the 43K molecular weight tail lead to less efficient anchoring of the surfactant to the polymer particles. Barrett examined this ASB effect in detail in conventional liquid organic solvents,[13] and this phenomenon was previously explored for the PS system in CO_2.[23,24] If the soluble block is much larger than the anchor block, there will be little driving force for adsorption to the surface of the polymer particles; this is undoubtedly the case for the PVAc-*b*-PFOA (4K/43K) block copolymer, which has a very low ASB. The relatively high solubility of the PVAc segment in CO_2 compared to other anchor groups used in stabilizers for dispersion polymerizations will further reduce its tendency to adsorb onto the surface of the polymer phase. Finally, even though the PFOA homopolymer has the highest molecular weight (~100 000) and is thus theoretically capable of stabilizing the largest surface area, it has little tendency to adsorb to the interface. The weaker adsorption of PFOA homopolymer stabilizer to the particle interface results in coalescence of unstabilized nuclei during the particle formation stage which in turn leads to larger particles.

Quantitative in Situ Particle Size and Sedimentation Measurements. The particle sizes were measured at the completion of the VAc dispersion polymerizations for latexes stabilized with either PFOA homopolymer or PVAc-*b*-PFOA (4K/43K). Because multiple scattering was present, the latexes were diluted by venting some of the latex out of the view cell at a constant pressure of 345 bar and then adding more CO_2 to the cell. This dilution procedure was repeated until the optical density was less than 1.0.

According to the Lorenz−Lorentz mixing rule, the refractive index of the polymer particles at the end of the reaction was estimated to be 1.39 ± 0.01, assuming that no monomer remains and that the PVAc particles were swollen 40% by CO_2 (based on the swelling measurement.) Due to the sinusoidal nature of the scattering coefficients with particle size, the turbidity ratio method gave multiple solutions of 3.9, 5.3, and 7.2

μm for the PFOA-stabilized latex and 4.2, 4.9, and 7.6 μm for the PVAc-*b*-PFOA (4K/43K)-stabilized latex. With other pairs of wavelengths (750 and 650 nm, 700 and 600 nm) very similar solutions were obtained. To discern the correct solution, the volume fraction was calculated for each solution and compared to the volume fraction determined by the degree of dilution, assuming 100% conversion and the above result for the amount of swelling by CO_2. The final average diameter for the PFOA homopolymer-stabilized reaction was found to be 7.2 μm, while the average diameter of the PVAc-*b*-PFOA (4K/43K)-stabilized particles was 7.6 μm. The error in the measurement was large, $\sim\pm$1.0 μm. In any case, these sizes are much larger than those of PMMA and PS particles produced by dispersion polymerization in CO_2 at similar conditions.[15,16,24,39,40]

The relatively large size of the PVAc particles when compared to PMMA or PS particles can be related to the higher solvent quality of CO_2 for PVAc compared to the other polymers. The growing polymer chain will reach a critical chain length in solution before nucleation takes place. As the solvent quality for the polymer is increased, the chain grows to a longer length in solution before nucleation. Consequently, supersaturation will develop more slowly, which in turn will lower nucleation rates.[41] Moreover, our result that the particle number decreases and particle size increases as the solvent quality is increased has been observed experimentally in many dispersion polymerizations.[42]

The volume fraction at the end of the reaction is $\sim$20% PVAc, assuming a particle phase-density of 1.0 g/cm^3. From the final particle sizes, the particle number density is 2.2×10^9 cm^{-3} for the PFOA-stabilized particles and 1.1×10^9 cm^{-3} for the PVAc-*b*-PFOA (4K/43K)-stabilized particles. These numbers are roughly in agreement with the maximum number of particles seen in Figure 3c, suggesting that the decrease in particle number density with time seen in all the curves results from the increasing contribution of multiple scattering. The actual particle number density appears to be determined within the first 20−30 min of the reaction.

By comparing the results in Figure 3c with those obtained for MMA dispersion polymerization in CO_2 at 4000 psi and 65 °C,[22] it can be seen that the maximum particle number density is $\sim$1 order of magnitude lower for PVAc than for PMMA. Both studies used approximately the same concentrations of monomer, surfactant, and initiator. The final PMMA particle size was $\sim$3.3 μm, as determined by SEM.

If it is assumed that the PVAc particle number density remains 1 order of magnitude lower than the PMMA particle number density throughout the particle growth regime, a simple geometrical argument can be used to predict the final particle size. In both reactions, the monomer concentration was $\sim$20 wt % monomer/CO_2; thus, the total volume fraction of particles is constant at the end of the reaction such that

$$r_2/r_1 = (N_2/N_1)^{1/3} \tag{4}$$

where N is the particle number density and r is the particle radius. Since the PMMA particle radius is $\sim$1.65 μm, the final PVAc particle diameter should be $\sim$7.1 μm, which is in agreement with the size calculated from the turbidity spectra at the end of the reaction.

The stability of the latex to sedimentation at the end of the reaction was monitored by turning off the stir bar and observing the sedimentation front. The latex stabilized by PFOA settled $\sim$6 mm in 15 min, giving a sedimentation velocity of 6.7×10^{-4} cm/s. In Stokes' law for the sedimentation velocity of a single particle, u_0, is given by

$$u_0 = (2\Delta\rho g r^2)/(9\mu) \tag{5}$$

where $\Delta\rho$ is the density difference between the particle and the continuous phase, r is the particle radius, and μ is the viscosity of the continuous phase. The viscosity and density of CO_2 are 8.0×10^{-4} P and 0.842 g/cm^3, respectively, at 345 bar and 65 °C. Assuming a particle-phase density of 1.0 g/cm^3, Stokes' law gives a sedimentation velocity of 4.1×10^{-3} cm/s for a 7.2-μm-diameter particle. For high-volume fractions, the settling velocity, u_s, is given by eq 6,[43] where ϕ is the volume fraction

$$u_s = u_0(1 - \phi)^K \tag{6}$$

of particles and K varies from 4.5 to 7.0. For particles with no interactive forces, K is equal to 6.55.[43] With 40 vol % swelling, the dispersed-phase volume fraction is 20%. With $K = 6.55$, eq 6 predicts a sedimentation velocity of 9.5×10^{-4} cm/s for 7.2-μm particles. The reasonably good agreement between the predicted and observed sedimentation velocity further supports the turbidimetric determination of particle size.

Turbidimetry Measurements on Dispersion Polymerizations with PDMS-Based Stabilizers. The average diameter, dispersed-phase volume fraction, and particle number density were also obtained for the PDMS-based surfactants as shown in Figure 4. Size calculations were possible for the first 80 min of the reaction due to the relatively low turbidities of these latexes. Overall, the particle diameters were much larger for the PDMS-based surfactants than with surfactants containing PFOA stabilizing blocks. The PVAc-*b*-PDMS block copolymer gave a slightly smaller particle diameter than the PDMS homopolymer initially, but it rapidly increased to >3 μm. As expected, the dispersed-phase volume fraction was significantly higher for the block copolymer versus the homopolymer. The block copolymer also stabilizes a slightly higher number of particles than the homopolymer. These results are consistent with visual observations that the latex stabilized by the PDMS homopolymer settles during the first 2 h of the reaction. In contrast, when PVAc-*b*-PDMS was used, no bulk PVAc phase was visible during the entire 2 h in which optical measurements were taken. However, the PVAc latex eventually collapses and precipitates to the bottom of the cell after $\sim$4.5 h. The larger particle diameters obtained with PDMS-based surfactants compared to PFOA-based surfactants result from the poorer solvent quality of CO_2 for PDMS.

Effects of Cosolvents, Pressure, and Stabilizer Concentration. In an effort to improve the performance of the PDMS-based stabilizers, small amounts of organic cosolvents were employed. In these experiments, the PVAc-*b*-PDMS diblock copolymeric stabilizer was used and 5% (v/v) of either *n*-heptane or 2-propanol was added to the initial reaction mixtures. The results from these experiments are shown in Table 3. Because these liquids are good solvents for PDMS, their addition to the reaction mixture should serve to prevent the

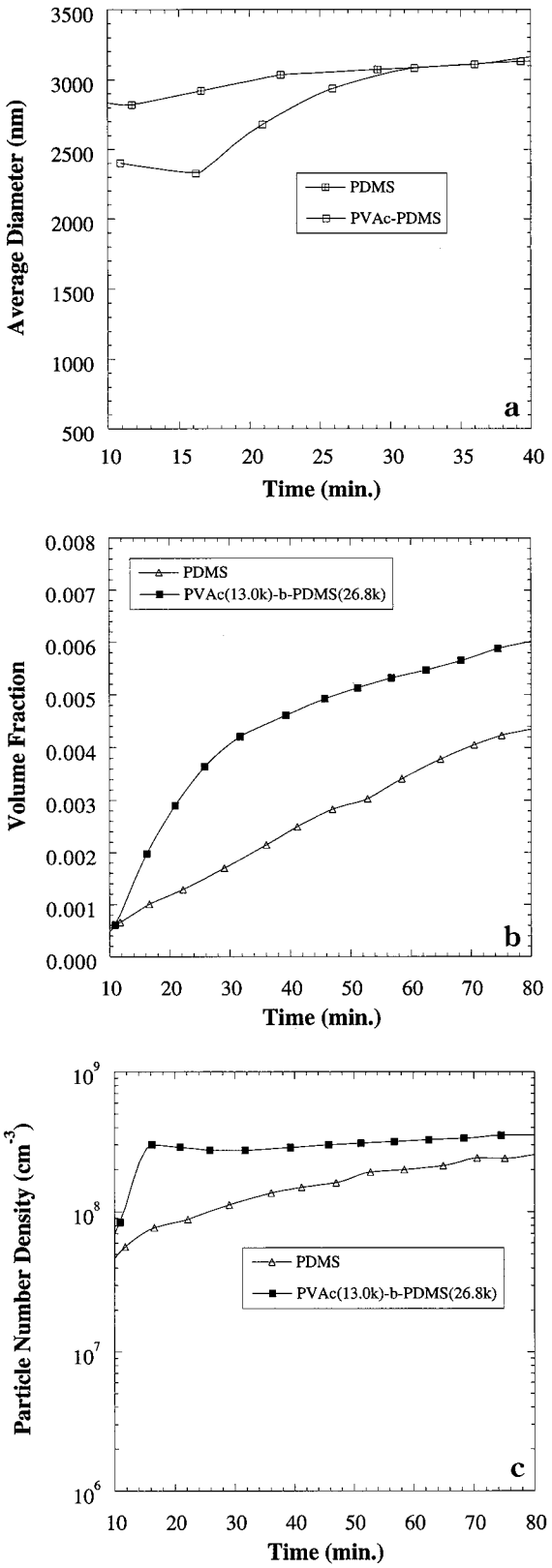


Figure 4. Dispersion polymerizations of VAc in CO_2 using PDMS-based stabilizers: (a) average particle diameter, (b) dispersed-phase volume fraction, and (c) particle number density.

collapse of the PDMS chains at high conversion. Indeed, the latexes formed during these reactions were stable for a longer period of time than when pure CO_2 was used, but at high conversions, flocculation of the particles was observed: macroscopic chunks of solid were visible in the cell. *n*-Heptane was qualitatively more effective than 2-propanol, probably because of the solubility properties of the PVAc. Ideally, the cosolvent in a dispersion polymerization should be a good solvent for the stabilizing layer but a poor solvent for the dispersed phase; *n*-heptane meets these criteria, while 2-propanol is a good solvent for both PVAc and PDMS.

Because properties such as the density and dielectric constant in supercritical fluids can be tuned by changing the pressure, the effect of variations in pressure was also studied (Table 4). For the precipitation polymerizations in the absence of stabilizer, as the pressure is increased molecular weights also increase. This makes sense because the more dense CO_2 at higher pressure will have a greater solvating power for the growing PVAc oligomeric radicals. Thus, the chains will grow to a longer length prior to the onset of precipitation. In this way, the critical molecular weight for precipitation of the polymer chains is effectively changed by simply tuning pressure. In addition, high pressure gives greater plasticization of the polymer phase which in turn leads to enhanced monomer diffusion within the polymer phase. When the PVAc-*b*-PFOA stabilizers were employed, no trends in yields or molecular weights were observed. This stands in stark contrast to the dramatic pressure effects, which have been reported in styrene disperison polymerizations,[24] but parallels reports that pressure changes in the range do not significantly effect MMA dispersion polymerizations in compressed CO_2.[16]

Finally, results from a study of the effect of the stabilizer concentration are shown in Table 5. Again, no quantitative trend in the polymer yield or molecular weight could be discerned from these studies. For stabilizer concentrations greater than or equal to 5 wt % (to monomer), stable latexes resulted. Although the focus of our experiments was not the quantification of sedimentation times, the latexes were qualitatively stable in the absence of stirring for some time frame longer than 5 min. In one experiment, the latex was found to be stable without stirring for more than 3 days. For stabilizer concentrations lower that 5 wt % (to monomer), however, the latexes were unstable and settled quickly in the absence of stirring. This parallels the observations made in the polystyrene/CO_2 system, where low amounts of stabilizer were shown to be insufficient for producing well-stabilized colloidal microspheres.[24]

Polymerizations in Liquid CO_2. Several initiating systems that are active at room temperature have been investigated in an effort to conduct polymerizations in liquid CO_2 at relatively low pressures. However, typical low-temperature initiators previously used in liquid CO_2, including the azo initiator WAKO V-70 and the organic redox system of benzoyl peroxide and dimethylaniline, did not efficiently initiate the polymerization of VAc and yields of polymer after 18 h were less than 5%. However, because charged redox initiating systems and thermal initiators such as diisopropylperoxy dicarbonate are used in industry to initiate VAc reactions at low temperatures, we continued to explore the use of other low-temperature initiators. Finally, an initiator that was very effective was discovered, diisobutyryl peroxide. This initiator has a 10-h half-life at 19−23 °C, and polymerizations of VAc were conducted in CO_2 at ~25 °C and a pressure of 155 bar. The results from these reactions are shown in Table 6. Yields for these

Table 3. Effect of Added Cosolvent on the Dispersion Polymerization of VAc in CO_2[a]

cosolvent	vol cosolvent (mL)	yield[b] (%)	M_n[c] (10^{-3})	PDI[d]	comments
2-propanol	0.5	72	11	3.2	unstable latex
n-heptane	0.5	82	48	3.6	unstable latex

[a] Conditions: pressure, 255 (±8) bar; temperature, 65 (±0.1) °C; 18-h reaction time; 0.2 g of stabilizer (PVAc-*b*-PDMS); 2.0 g of VAc monomer. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n).

Table 4. Effect of Pressure on the Polymerization of VAc in CO_2

stabilizer	stab wt (g)	P_{init}[a] (bar)	temp (°C)	time (h)	yield[b] (%)	M_n[c]	PDI[d]
none	0	147	65	4	42	19	2.0
	0	217	65	4	46	35	2.5
	0	354	65	4	52	49	2.6
	0	175	65	18	80	12	4.0
	0	219	65	18	91	21	2.4
	0	345	65	18	78	24	2.4
PVAc-*b*-PFOA[e]	0.2	194	65	18	90	45	4.2
	0.2	220	65	18	97	25	3.8
	0.2	359	65	18	91	70	3.3
PVAc-*b*-PFOA[f]	0.1	54	25	18	91	43	2.4
	0.1	198	25	18	100	39	2.3
	0.1	343	25	18	98	36	2.5

[a] P_{init}, initial pressure. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n). [e] M_n PVAc block, 4.4×10^3; M_n PFOA block, 4.3×10^4. [f] M_n PVAc block, 1.0×10^4; M_n PFOA block, 4.3×10^4.

Table 5. Effect of Stabilizer[a] Concentration of the Dispersion Polymerization of VAc

stabilizer wt (g)	yield[b] (%)	M_n[c]	PDI[d]	comments
0.4	78	26	2.4	stable latex
0.2	90	51	4.3	stable latex
0.1	86	29	2.5	stable latex
0.05	96	44	3.5	unstable latex
0.025	90	45	3.4	unstable latex

[a] Stabilizer, PVAc-*b*-PFOA (10K/43K). [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n).

reactions were quantitative even in the absence of stabilizer, and again the PFOA-based stabilizers resulted in the most stable latexes. Because of the low T_g of the material, which is exacerbated by the plasticization with CO_2, isolation and analysis of the particles was difficult. Others have also noted that extensive particle melting and deformation occurs during PVAc sample preparation for SEM.[8]

Copolymerizations of Ethylene and VAc. Three different compositions of EVA copolymers were prepared by polymerization in supercritical CO_2. The results from these experiments are shown in Table 7. In addition to unstabilized precipitation control reactions, PDMS homopolymer (the ideally inexpensive stabilizer) and PVAc-*b*-PFOA diblock copolymer (the most effective stabilizer identified thus far) were compared.

Rindfleisch and co-workers have shown that ~5% (w/w) PE (M_w = 108 500) is insoluble in CO_2 even at 270 °C and 2750 bar.[29] Thus, high-molecular-weight PE has very low solubility in CO_2 at the reaction conditions employed,[29] and as a result, homopolymerization of ethylene monomer at the conditions employed herein gave very low yields of polymer (<5%). These results parallel earlier work by Kagiya and co-workers in liquid and supercritical CO_2 which gave similarly low conversions of PE.[44] These authors also demonstrated that the polymer molecular weight is depressed by the addition of CO_2 and that CO_2 does not act as a chain-transfer agent and has no effect on initiation when ethylene polymerizations are initiated by AIBN.[45]

In comparison, the EVA copolymers, which had an ethylene content of ~65 mol % (by ^{1}H NMR), were produced in ~65−75% yield. In this case, the addition of VAc comonomer dramatically improves the results. Again, the PVAc-*b*-PFOA-stabilized reactions resulted in qualitatively stable latexes for all of the comonomer compositions studied, while the PDMS-stabilized reactions gave rise to unstable latexes which collapsed near the end of the reaction. It should be noted that GPC results are not particularly meaningful for these copolymers due to the low solubility of PE in the mobile phase.

Reported copolymer compositions were determined by ^{1}H NMR analysis of the resulting products: δ = 0.85 (t, 3H, methyl group from PE branches), 1.2 (s, br, 2H, methylene from PE repeat units), 1.3 to 1.8 (multiplet, 2H, methylene from PVAc repeat units), 2.0 (s, 3H, methyl group from PVAc repeat units), 4.8 (s, br, 1H, methine from PVAc repeat units), 7.24 (s, 1H, $CHCl_3$ from solvent reference peak).

Conclusions

The dispersion polymerization of vinyl acetate and copolymerization of vinyl acetate and ethylene in a CO_2 continuous phase has been investigated. The effectiveness of stabilizers of various chemical compositions and architectures was compared. Both fluorinated and siloxane-based stabilizers including homopolymers, block copolymers, and reactive macromonomers were employed. When the appropriate stabilizer was used, the reactions resulted in high conversion of polymer, and the final reaction mixtures existed as stable latexes of PVAc or EVA in liquid or supercritical CO_2. The initiator diisobutyryl peroxide was determined to be very effective for the initiation of VAc monomer in liquid CO_2 at room temperature. The use of organic cosolvents to increase the stability of PDMS-stabilized latexes was investigated. The effects of variation in the concentration of stabilizer, stabilizer anchor-soluble balance, and pressure on the resulting PVAc products were studied.

Table 6. Comparison of Stabilizers for the Polymerization of VAc in Liquid CO_2

entry	stabilizer	stab wt (g)	time (h)	yield[b] (%)	M_n[c]	PDI[d]	comments
1	none	0	18	96	34	2.6	product settles
2	PDMS homopolymer[e]	0.1	18	90	46	2.5	product settles
3	PFOA homopolymer	0.1	18	100	39	2.6	stable latex
4	PVAc-*b*-PDMS	0.1	18	97	39	2.6	product settles
5	PVAc-*b*-PFOA[f]	0.1	18	100	39	2.3	stable latex

[a] Reaction conditions: 2.0 g of VAc; 2.4×10^{-2} M diisobutyryl peroxide; $P = 155$ (±24) bar; $T = 27.0$ (±1.0) °C. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n). [e] Viscosity, 10 000 cSt. [f] M_n PVAc block, 1.0×10^4; M_n PFOA block, 4.3×10^4.

Table 7. Copolymerizations of Ethylene and VAc in CO_2

stabilizer	[VAc] (mol %)[a]	[ethylene] (mol %)[a]	yield[b] (%)	M_n[c] (10^{-3})	PDI[d]
none	83.0	17.0	77.2	13	4.5
	64.7	35.3	81.2	11	3.7
	35.7	64.3	66.4	21	2.8
PDMS homopolymer	80.2	19.8	82.1	32	4.1
	65.0	35.0	82.9	19	4.7
	33.7	66.3	67.7	12	5.4
PVAc-*b*-PFOA	84.8	15.2	72.0	39	10
	63.5	36.5	73.9	8.4	15
	38.0	62.0	76.5	14	33

[a] Copolymer mole percent compositions were determined by ^{1}H NMR. [b] Yields were determined gravimetrically. [c] M_n, number-average molecular weight distribution. [d] PDI, polydispersity index of the molecular weight distribution (M_w/M_n).

The in situ turbidimetry technique was used successfully to monitor dispersed-phase volume fractions, particle sizes, and number densities during the polymerizations and to give the final particle sizes at the end of the polymerizations. When the PFOA-based stabilizers were compared, the maximum particle density in the particle formation stage was highest for PVAc-*b*-PFOA (31K/54K), somewhat lower for PVAc-*b*-PFOA (31K/20K) and PFOA homopolymer (~100K), and lowest for PVAc-*b*-PFOA (4K/43K). For the PFOA homopolymer and PVAc-*b*-PFOA (4K/43K) diblock copolymer, the anchor-soluble balance was too low to give sufficient adsorption during the particle formation stage. Compared with the PFOA-based stabilizers, the PDMS-based stabilizers produced larger particle sizes and lower number densities during the particle formation stage, consistent with the lower solvent quality of CO_2 for PDMS. The PDMS-based surfactants were incapable of stabilizing the latex throughout the reaction in the absence of cosolvent.

The change in the dispersed-phase volume fraction with time was very similar for all the PFOA-based stabilizers, as well as for the PVAc-*b*-PDMS during the first hour of the reaction, demonstrating that the reaction kinetics at low conversion are not significantly affected by the type of surfactant used. Particle size measurements at the completion of the reaction showed that much larger particles are obtained for PVAc compared to other polymer colloids previously produced in CO_2. The larger particle size for PVAc may be attributed to the higher solvent quality of CO_2 for PVAc compared to PMMA and PS, which lowers the degree of supersaturation. Consequently the nucleation rate decreases, resulting in fewer nuclei and ultimately larger particles. The final particle number density agreed with the maximum particle number density measured in the first 40 min of the reaction, suggesting that the particle number density is fixed early in the reaction.

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