Surfactant-Free Emulsion Polymerization of Chlorotrifluoroethylene with Vinylacetate or Vinylidene Fluoride

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ABSTRACT: A surfactant-free emulsion process has been developed for the preparation of copolymers of chlorotrifluoroethylene with vinylacetate or vinylidene fluoride. A redox initiator system, consisting of sodium-meta-bisulfite, t-butylhydroperoxide, and ferrous sulfate heptahydrate, has been found to be effective in preparing self-emulsifying fluoropolymers with a monodisperse particle size distribution, having up to 45% polymer solids in water. Over the range studied in this investigation, the particle number and the ultimate particle size is linearly related to the quantity of initially charged redox catalyst. Under conditions of optimal catalyst concentrations, a greater number of particles is produced in the surfactant-free process than that which can be obtained using conventional fluorosurfactants. Particle number is defined at the earliest stage of polymerization and remains constant throughout the polymerization, unless surfactant is postadded to the surfactant-free latex at a very early stage in the polymerization. The aqueous phases of various latices have been purified by ionexchange and dialysis, enabling the sulfonic acid-terminated fluoropolymer end groups to be quantified. The highest level of bound sulfonic acid is obtained at elevated temperatures. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2211–2225, 1998

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INTRODUCTION

Polychlorotrifluoroethylene (PCTFE) has been a commercial resin since the 1950s. However, its availability has been limited to powder, pellets, and film. As a member of the fluoropolymer family, PCTFE film has found utility due to its exceptional moisture barrier properties and transparency (UV/VIS).^{1,2} Unlike PTFE, PCTFE is a transparent melt processable fluoropolymer. When compared to other transparent fluoropolymers such as perfluorinated poly(ethylene-hexafluoropropene), or the perfluorinated polyal-

kylvinylethers (PFA), PCTFE is distinguished by a lower coefficient of expansion, higher tensile strength, higher tensile modulus (4–6 times), and much lower gas and moisture permeability. Using aqueous dispersion grades of PCTFE and related copolymers, inflammable, transparent barrier fluoropolymer coatings can be obtained that can be fused onto substrates from 100–250°C. This enables the coating of low melting substrates such as plastics, which is inconceivable for PTFE, PFA, E-CTFE, and FEP, which must be fused onto substrates from 260–375°C.

One objective of this investigation was to design a surfactant-free emulsion process for the preparation of copolymers containing chlorotrifluoroethylene (CTFE). Investigations have focused on copolymers of CTFE containing less than 50%

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by weight of vinylidene fluoride (VDF) and/or vinylacetate (VAC). Emulsion particles have been prepared having bound sulfonic acid groups. The process has good control over particle number density (number of particles/liter of latex) and particle charge density, which is a tremendous advantage in the preparation of stable high solids surfactant-free emulsion particles. Charged emulsion particles, protected by an electric double layer, containing upwards of 50% polymer solids in water have been prepared in the absence of functional ionic monomers such as ethylenesulfonic acid, 2-sulfoethylmethacrylate, and the like, all at a conversion rate that compares favorably to conventional emulsion polymerization. This is in stark contrast to other emulsifier-free formulations using metal persulfates that tend to yield latices having low solids contents, slow conversion rates, and small surface charge densities.³ Another characteristic of surfactant-free emulsion polymerization is that generally the particle number density is an order of magnitude lower than that obtained by emulsion polymerization employing surfactants. This is probably related to the lower total polymer surface area, which can be stabilized by less disassociated ionic functional groups such as the sulfate residues from metal persulfates, and the instability of the sulfate functionality.4,5 Sulfate terminated nonfluorinated chain ends hydrolyze with time, generating hydroxyl functionality that can subsequently oxidize to carboxylic acid groups.

Although most investigations of surfactantfree emulsion systems have used the well-known metal persulfate free radical initiator system, other researchers have recognized the drawbacks of the persulfate system and have attempted to synthesize latices rich in nonhydrolyzable sulfonic acid. Strategies include, for example, the use of sulfonate-containing peroxide initiators such as disodium bis(4-sulfomethyl benzoyl peroxide),⁶ or the use of redox systems such as bisulfite/Fe³⁺. The former requires the synthesis of novel peroxides, while the latter requires the use of high levels of iron (III).⁷ An additional strategy is the use of bisulfite with potassium persulfate, which has been shown by other investigators to yield stable emulsions rich in sulfonic acid end groups.⁸ Although the persulfate/bisulfite redox system is used commercially, it has been relatively neglected in the literature. This has been attributed to the uncertainty of the surface functionality generated, and the free radical processes involved.9-12

The surfactant-free emulsion process used in this investigation is carried out using a redox, free radical initiating system consisting of sodium-*m*-bisulfite (SmBS), ferrous sulfate heptahydrate, and *t*-butylhydroperoxide (*t*-BHP), which are all water soluble. In contrast to the metal persulfates, which generate sulfate radicals at elevated temperatures that are prone to hydrolysis, SmBS, in the presence of an oxidizing agent, yields the bisulfite radical conveniently at room temperature or lower, which ultimately leads to emulsion particles rich in sulfonic acid-terminated polymer chain ends. The use of an oxidizing agent such as *t*-BHP eliminates the need for high levels of ferric iron.

Sulfonic acid-terminated *fluoropolymers* are even stronger acids than their hydrocarbon derivatives, and are completely disassociated at high and low pHs, producing stable latices over the entire pH range. Redox catalyst quantity, its mode of addition, polymerization temperature, and comonomer, all impact the concentration of emulsion particles that can be obtained. All indications suggest that this polymerization follows the process known as homogeneous nucleation.

According to the theory of homogeneous nucleation, when using a water-soluble free radical source, an ionic free radical generated in the aqueous phase adds to a monomer, yielding a sulfonic acid-terminated fluorocarbon radical.^{13,14} As more fluoromonomer units are added, the length of the sulfonic acid-terminated fluorinated alkyl oligomer is extended. Until a critical chain length is achieved, the charged oligomer is water soluble, after which micelle formation occurs. The structure of the charged oligomer is probably similar to that of a fluorosurfactant. At the beginning of polymerization, when free radicals are first generated in the presence of monomer, a large quantity of charged ionic species is generated simultaneously. When these growing oligomers become too hydrophobic, and when their concentration in water is high enough, such that the critical micelle concentration (CMC) is reached, they are forced out of the aqueous phase. The oligomers coalesce into spheres (micelles) having a hydrophobic interior emulsified in water by ionic chain ends. A monodisperse distribution of small particles (micelles) is created. Monomer then swells the newly created particles. As charged oligomeric radicals are subsequently created in the aqueous phase, various outcomes are possible: (1) although the newly created emulsion particles are small in size, their number is large such that they have tremendous surface area. Newly created charged oligomeric species readily absorb onto the surface of an existing particle, providing a free radical source to the monomer rich particle. (2) Charged oligomeric species may collide in the aqueous phasewasting initiator. However, such collisions lead to surfactant-like molecules that can absorb onto the surface of existing particles. (3) Additional quantities of charged oligomeric radicals coalesce into additional particles in the presence of the existing particles to generate a second distribution of particles.

This last option is unlikely, ensuring that a monodisperse distribution of particles will persist. After creation of the first generation of particles, rapid growth in size occurs, increasing their surface area. With time it becomes increasingly unlikely that a second crop of particles can be created. This can only be achieved if instantaneously a sufficient quantity of charged oligometric free radicals is created to (1)cover the surface of the existing particles, and (2) exceed the CMC for a second time, thus generating a second generation of micelles. For these reasons, surfactant-free polymerization can be expected to lead to monodisperse particles having a narrow particle-size distribution. Proof that particle nucleation does not reoccur can be obtained by measuring the particle-size distribution as a function of time. However, using the SmBs/t-BHP/Fe surfactant-free system, it has been found that fluorosurfactants can be added after homogenous nucleation has occurred to (1) cause particle nucleaton to reoccur, and (2) obtain a particle density that far exceeds that which can be obtained by fluorosurfactants alone, using similar concentrations of fluorosurfactant.

To quantify the charge on the surface of the emulsion particles, the latices have been ion exchanged and treated by dialysis. Because the surface active agents are chemically bound to the fluoropolymer particle, the aqueous phase can be purified without danger of particle flocculation. Deionization of the latices leaves only a small ionic residue that corresponds to a chemically bound surface charge. After purification of the aqueous phase, simple titration can be used to characterize the amount of bound surface charge.



Figure 1 Pressure and solids concentration (% solids) as a function of time for a PCTFE/VAC copolymer (latex 1).

EXPERIMENTAL

Polymer Synthesis

Latex 1

To a 1 gallon vertically disposed stainless steel reactor was charged 2.3 L of deionized (DI) water and 650 g CTFE. Unless indicated, all water used in this study was DI/deoxygenated water. At room temperature, the autoclave was filled with nitrogen, then evacuated; a process that was repeated seven times. The autoclave was heated to 43.8°C yielding a pressure of 152.1 psig (1.05 MPa). t-BHP was obtained from the Aldrich Chemical Co. at a 70% concentration in water. The initial initiator solutions were prepared as follows: (1) 1.43 g of the *t*-BHP solution was diluted to 250mL with DI water, (2) 1.24 g SmBS was diluted to 250 mL with DI water. To initiate polymerization, both solutions were separately charged to the vessel at a rate of 2.4 mL/min for 20 min. Thereafter, the redox agents were charged at a slower rate, 0.33 mL/min. The emulsion polymerization was conducted using an agitator consisting of two flights of four pitched blades having an axial flow geometry, rotating from 350-700 rpm. The polymerization was started with a high agitation rate that was gradually reduced with increasing concentration of emulsified polymer solids. During the slow addition of redox initiator, 72 g of vinylacetate was charged at 0.24 g/min. After 5 h, the autoclave was then vented at 34.1 psig, yielding a dispersion having 20% polymer solids. A sample was withdrawn from the autoclave at the time intervals shown in Figure 1.

Latex	3	4	5	6	7
CTFE (initial charge/g)	300	350	360	75	75
VDF (initial charge/g)	10	12	30	8	6
Deionized water (L)	1.1	1.1	1.6	1.7	1.3
$Fe(SO_4)_2 \times 7H_2O$	0.1	0.15	0.3	0.22	0.22
Initial charge SmBS (g; ppm)	0.13; 118	0.63;572	0.92;575	1.50;882	1.18;907
Initial charge <i>t</i> -BHP (g; ppm)	0.11;100	0.52;473	0.83; 519	1.25;735	0.98; 754
Addition time SmBS (initial charge, min)	40	20	10	10	10
Addition time <i>t</i> -BHP (initial charge, min)	40	20	10	10	10
SmBS added in first 10 min (g; ppm)	0.03; 30	0.32;286	0.92;575	1.5;882	1.18;907
Final particle diameter (microns)	0.3	0.31	0.24	0.23	0.24
Particle number $(\times 10^{16})$	2.76	4.58	8.54	9.53	9.02
Particle number/L charged water ($\times 10^{16}$)	2.51	4.16	5.33	5.6	6.94
Average conversion rate (g/min)	2.55	3.88	5.33	3.76	6.94

 Table I
 Polymerization Conditions, Particle Number Density, Particle Size, and Conversion Rates

 for Surfactant-Free PCTFE/VDF Latices 3–7

Latex 2

To a 30 gallon glass-lined autoclave was charged 22 gallons of DI water, 9.3 kg of CTFE, and 0.7 kg of VDF. The temperature was maintained during the polymerization from 15–25°C, the resulting pressure ranging from 30-130 psig. Initial charges of two separate redox initiator streams were added simultaneously to the autoclave at a rate of 50 mL/min over a 10-min period: (1) 80 g of a solution of 70 wt % of a *t*-BHP solution diluted to 500 mL with DI water; and (2) 62.16 g SmBS and 12.61 g ferrous sulfate heptahydrate diluted to 500 mL with deionized water. After the addition of the initial charges of redox initiator, two additional, separate continuous charges (288 g of the t-BHP solution and 235 g of the SmBS solution, each diluted to 2 L with DI water) were then supplied simultaneously and continuously into the autoclave from two separate reservoirs at a rate of 5.5 mL/min, respectively, for the duration of the polymerization. After consumption of the initial charge of monomer, 45.97 kg of CTFE and 1.42 kg of VDF was added in increments to the autoclave to maintain the pressure as described, after which 22.39 kg of CTFE and 4.34 kg of VDF was added in a similar fashion, yielding a total of 77.66 kg of charged CTFE and 4.34 kg of charged VDF: 1320 mL of a 20% solution of ammonium octanoate in water was bombed into the autoclave over a 5-s period 80 min after the initial charging of polymerization initiator. The autoclave was vented after 8 h yielding a dispersion having 49% polymer solids in water. Five samples of dispersion were withdrawn through a bottom discharge

valve during polymerization at the time intervals indicated in Figures 3 and 4. The dependence of polymer solids, particle diameter, and particle number, are shown in Figures 3 and 4. Attempts to obtain dispersion samples at later stages of conversion yielded only a semifoamed, coagulated product.

Latices 3–7

The polymerization conditions are summarized in Table I. A 3.8-L stainless steel autoclave was charged with 1.1 L of DI water (latex 3). The autoclave was then charged with 300 g of CTFE and 10 g of VDF and the temperature increased to 40°C yielding a pressure of 172 psig. Initial charges of two separate redox initiator streams were added simultaneously to the autoclave at a rate of 1.25 mL/min over a period of 40 min: (1) 0.15 g of a solution of 70 wt % of a *t*-BHP solution diluted to 50 mL with DI water; and (2) 0.128 g SmBS and 0.3 g ferrous sulfate heptahydrate diluted to 50 mL with deionized water. After the addition of the initial charges of redox initiator, two additional, separate continuous charges (5.77 g of the t-BHP solution and 4.88 g of the SmBS solution, each diluted to 200 mL with DI water) were then supplied simultaneously and continuously into the autoclave from two separate reservoirs at a rate of 0.25 mL/min, respectively, for 5 h. The temperature was held between 40–45°C. Independent streams of CTFE and VDF were also continuously fed into the autoclave at a rate of about 10 g/min and 0.5 g/min, respectively, to maintain an internal pressure between 140 and

Latex	${{\rm SO_4^{-2}}}\ (\mu { m g/mL})$	Oxalate	% Polymer	Time
(Ratio Bisulfite: <i>t</i> -BHP)		(µg/mL)	Solids	(min)
$\begin{array}{c} (8) \ (1.07:1) \\ (9) \ (0.98:1) \\ (10) \ (1.03:1)^{\mathrm{a}} \end{array}$	1340 1300 1610	trace (<1) 16–18 65–70	$ 41.3 \\ 41.9 \\ 42.4 $	304 295 360

Table IIDependence of Oxalate and Sulfate Levels on t-BHP and SmBSStoichiometry for Surfactant-Free PCTFE/VDF Latices 8–10

^a An alternating large excess of SmBS or *t*-BHP.

180 psig. After a total of 5 h, a total of 950 g of CTFE and 32 g VDF had been added to the autoclave. The reactor was vented at a pressure of 80.6 psig, yielding a latex containing 36% polymer solids, 766 g of PCTFE/VDF copolymer.

Latices 8–10

Redox initiator stoichiometries are summarized in Table II. A 10-gallon glass-lined autoclave was filled with 5 gallons of DI water. To this was charged 2.54 kg of CTFE and 126 g of VDF. The temperature of the autoclave was held between 40-45°C. The agitator consisted of two flights of three axially pitched blades. The agitation rate was reduced gradually from 300 to 150 rpm. Two separate solutions of redox initiators were charged to the autoclave over a 10-min period; (1) 18.34 g of a 70% solution of *t*-BHP was diluted to 100 mL with DI water, and (2) 15.45 g SmBS with 2.23 g ferrous sulfate heptahydrate diluted to 100 mL with DI water. Two separate solutions of redox initiators were then charged at a much slower rate of 83 mL/h; 65.5 g of a 70% solution of *t*-BHP diluted to 500 mL, and 51.2 g SmBS diluted to 500 mL. A total of 12.8 kg of CTFE and 0.85 kg of VDF was charged to the autoclave. After 304 min the autoclave was vented at 49.3 psig, yielding a dispersion containing 41.3% polymer solids.

Latices 11-14

Surfactant addition is summarized in Table III. The preparation of latex 11 is described as a general example. A 1-gallon stainless steel autoclave was charged with 1.1 L DI water. To this was added 350 g CTFE and 12 g VDF. The autoclave was heated to 42.5°C, yielding a pressure of 171.6 psig. Two separate redox solutions were charged to the autoclave over a period of 20 min to initiate polymerization (0.74 g *t*-BHP solution diluted to 50 mL, and 0.63 g SmBS combined with 0.15 g ferrous sulfate heptahydrate). After this initiation, 3.08 g SmBS and 3.96 *t*-BHP solution were separately diluted to 200 mL with deionized water and were charged at a rate of 33 mL/h. To maintain a pressure between 160–200 psig,

Latex	Time (min) ^a	${f Total} {d_w}^{ m b}$	Peak 1 d_w	Peak 1 wt (%)	$\operatorname{Peak}_{d_w} 2$	Peak 2 wt (%)	Particle Number/L ^c Latex	Surfactant (ppm) ^d
			0.308					
11	102//10	0.308	(0.30–0.32) 0.106	100	0 0.237	0	2.0	22727
12	17//4	0.197	(0.07-0.15) 0.196	31	(0.18 - 0.30)	69	6.1	5208
13	1//7	0.196	(0.07-0.37) 0.098	100	0 0.206	0	5.6	2083
14	2//1	0.146	(0.07 - 0.13)	55	(0.16 - 0.25)	45	13.4	2272

Table IIIDependence of Particle Size and Distribution on Time of Postadded Surfactant Additionfor Latices 11-14

^a Time elapsed from complete addition of initial redox initiators//minutes of addition.

^b Weight-average particle diameter (distribution range), microns.

 $^{c}(\times 10^{16}).$

 $^{\rm d}$ Based on initial charge of deionized water.

Latex	<i>T</i> /°C	CTFE (wt %)	VDF (wt %)	VAC (wt %)	Vinylpropionate (wt %)	NaOH Molar eQw/kg Polymer
17	45	78.0	22.0	0	0	0.007
18	42	91.0	9.0	0	0	0.005
19	100	91.4	8.6	0	0	0.011
20	15 - 25	93.3	1.6	5.1	0	0.003
21	15 - 25	91.3	5.0	0	3.7	0.003

Table IVDependence of NaOH Molar Equivalents of Sulfonic Acid Terminated Fluoropolymerfor Latices 17-21 on Polymerization Conditions

four additional charges of monomer were used, 350 g of CTFE and 14 g VDF each. One hundred two minutes after the complete addition of the initial charge of redox initiators, 25 g of lithium perfluorooctyl sulfonate diluted to 100 mL was added. After 420 min, a pressure of 73.1 psig was obtained and the autoclave was vented, yielding a fluoropolymer dispersion having 49% polymer solids.

Latex 15

A 3.8-L stainless steel autoclave was charged with 1.2-L of DI water. After adding 10 mL of a 25% solution of ammonium perfluorooctonoate in water, the autoclave was heated to about 41.5°C. The autoclave was then charged with 228 g CTFE and 23 g VDF, yielding a pressure of 190.6 psig. The initial and continuous charges of polymerization initiator were then pumped into the autoclave as described for latices 10-13. To maintain a pressure between 100–200 psig, two similar batches of CTFE and VDF were charged to the autoclave. After the polymerization reaction proceeded for 162 min, the pressure decreased to 58 psig and the autoclave was vented. The fluoropolymer dispersion contained 33% polymer solids, and had an approximate conversion rate of monomer to polymer of 4.2 g/min.

Latex 16

Latex 16 was prepared in a similar fashion to latices 11–14, with the exception that no surfactant was used. Six identical monomer charges were used, 200 g of CTFE and 10 g of VDF. After a total of 83 mL of *t*-BHP solution from the continuous charge had been injected into the autoclave, 0.833 g of succinic acid peroxide was added to the autoclave at a rate of 0.005 g/min, by addition to the *t*-BHP reservoir. After 258 min, the autoclave was vented, yielding a latex containing 48% polymer solids in water.

Latices 17–19

The polymerization conditions are summarized in Table IV. DI water (1.4 L) was charged to a 1-gallon stainless steel autoclave (latex 19). To this was added 360 g CTFE and 34 g VDF. The initial charges of redox initiator was added at 45°C over a 10-min period (1.2 g of a 70% t-BHP solution diluted to 50 mL, 1.0 g SmBS and 0.3 ferrous sulfate heptahydrate diluted to 50 mL). The temperature was raised to 100°C. 9.2 g of t-BHP solution, and 7.0 g SmBS were separately diluted to 100 mL and charged at a rate of 0.33 mL/min. Polymerization time was 223 min, yielding a latex having 39.4% polymer solids in water. Five hundred grams of a commercial sulfonic acid hydrogen ion exchange resin, Purolite C150TLH, available from the Purolite Company, was added directly to the latex (a large excess). The mixture was agitated for 1 h, after which the ion exchange resin was filtered away. Prior to use, the ion exchange resin was thoroughly treated with sulfuric acid and copious amounts of deionized water. A sample of 50 g of purified latex was then charged into a cellulose ester dialysis membrane (32-mm flat tube) having a molecular weight cutoff of 6-8,000. The tube was clamped on both ends and submerged into a 1-L reservoir of deionized water. The water was exchanged daily with deionized water. This procedure was repeated until a 1-day conductivity measurement of the reservoir was equivalent to deionized water. A sample of 25 g of the latex was then titrated with a 0.05%solution of sodium hydroxide.

Latices 20-21

The following is a general procedure for the terpolymerization of CTFE, VDF, and either vinylacetate or vinylpropionate, the conditions of which are summarized in Table IV. Five gallons of DI water were charged to a 10-gallon glass-lined au-

toclave. To this was added 2.28 kg CTFE and 225 g VDF. The initial charges of redox initiator was added over a 10-min period (20.36 g of a 70%) t-BHP solution diluted to 100 mL, 15.91 g SmBS, and 2.25 g ferrous sulfate heptahydrate diluted to 100 mL). After the initial charge of polymerization initiator, 350 g of an aqueous solution of perfluorinated ammonium octanoate was charged (20 wt % surfactant) over a 1-min period. t-BHP solution (109.06 g) and 85.2 g SmBS were separately diluted to 750 mL and charged at a rate of 2.0 mL/min. Twenty minutes after the continuous charge of initiator had been pumping, vinylpropionate was pumped into the autoclave at a rate of 4-5 mL/min, at a rate corresponding to the consumption of CTFE and VDF, to achieve a homogeneous incorporation of vinylpropionate into the terpolymer. Five additional batches of CTFE and VDF were added to the autoclave, 3.15 kg and 117 g, respectively. The autoclave was vented at 83 psig after 288 min of polymerization yielding a latex having 39.4% polymer solids in water. The latices were purified and titrated as in examples 17 - 19.

Physical Characterization

Elemental Analysis

A 50-g quantity of dried polymer was added to a 250-mL platinum flat-bottom dish and heated to 200°C (until the polymer melted). The heat was gradually raised to 375°C until the material charred and offgassing ceased. The polymer was then placed into a 450°C muffle furnace until no carbonaceous materials remained, approximately 60–90 min. To the cooled dish was added 20 mL of trace metal high-purity concentrated HCl, which was then heated until dissolution occurred. The contents were transferred to a 100-mL volumetric flask, to which 5 mL of concentrated hydrofluoric acid was added. The flask was then diluted to 100 mL. A similar acid solution was prepared and used as a blank. Sodium and iron were analyzed using atomic absorption spectroscopy (AAS) with a Varian Spectra AA200 instrument at the absorption lines of 589.6 and 248.3 nm, respectively. Silicon analysis was conducted using inductively coupled plasma (ICP; argon) with a Fisons ARL 3580 instrument at the emission wavelength of 251.6 nm.

Photon Correlation Spectroscopy

Photon correlation spectroscopy measurements were made with a custom-built Langley-Ford

LSA-II spectrometer. The light source was either a 647.1 nm Krypton laser or a 488 nm Argon ion laser. The scattered light was collected at a scattering angle of 90° and sent by fiber optics to an EMI photomultiplier tube. The resulting signal was digitized with an LFI pulse-amplifier discriminator and the correlation function was collected on a 256channel LFI Model 1096 correlator. All measurements were made on samples diluted in filtered water at 20°C (with a solvent refractive index of 1.333 and a solvent viscosity of 1.00 cp). The samples were diluted until the ratio (b/a) of the amplitude to the baseline of the correlation function was about 0.3, indicting that there was no significant amount of multiple scattering; for typical emulsions, this requires about a thousand-fold dilution. Ten correlation functions were collected for each sample, which were then combined (after eliminating any functions with abnormally high baselines) to yield a single normalized correlation function. The size distributions were then found by doing a numerical inverse Laplace transform on the normalized correlation function, assuming Raleigh-Gans scattering from solid spheres; the program used was a modified version of CONTIN.¹⁵ Particle number was calculated from the particle diameter according to the following equation: yield of polymer (mass, g) = volume of particle $(4/3)\pi r^3 \times polymer$ density $(2.0 \text{ g/cm}^3) \times \text{total number of particles. A}$ density number of 2.0 g/cm³ has been assumed for the latices having from 1-10% comonomer and likely represents an error of less than 5%.

Ion Chromatography

All ion chromatographic separations were performed on a Dionex 4000I ion chromatograph equipped with an AI-450 software package for postrun calculations. Separations were carried out using an AG4A guard column and AAS4A separator column. The eluent consisted of a 0.0017-*M* NaHCO₃/0.0018-*M* Na₂CO₃ at a 2.0 mL/min flow rate. A 50 μ L injection loop was used. Eluent suppression was accomplished using an Anion Micromembrane Suppresser (AMMS) and 0.05 *M* H₂SO₄ as regenerant at 6–8 mL/min. All samples were clarified before analysis using a high-speed centrifuge.

Scanning Electron Microscopy

SEM was conducted using a JEOLG300F Field Emission SEM on a sample of the latex that had been extremely diluted with deionized water, evaporated onto a glass coverslip, air dried, and sputtered with gold/palladium using a Denton Desktop II for 30 s. The accelerating voltage was 5 kV, and the working distance was 6 mm.

RESULTS AND DISCUSSION

Homogeneous Particle Nucleation

Initial investigation of the mechanism of the surfactant-free polymerization of CTFE containing polymers focused on a CTFE/VAC copolymer. However, all emulsion polymerizations were all carried out in a similar fashion. In a typical preparation, fluoroolefin(s) is first charged to a sealed pressure vessel containing deionized water. An initial injection of concentrated redox solutions is introduced into the vessel to initiate polymerization. The initial injection of redox agents typically represents 10–30% of the total amount of redox agents to be charged, and is charged within a short time frame of about 10 min. This is defined as the initial charge of polymerization initiator. After the initial charge of the polymerization initiator and the formation of (micelles) emulsion particles, a slow continuous charge of initiator takes place to: (1) allow particle growth to occur, and to (2) define the molecular weight of the final polymer. The slow continuous charge of initiator may take place over a period from 2–10 h.

For the preparation of latex 1, after an initial charge of CTFE, followed by an initial charge of redox agents and particle nucleation, vinylacetate was slowly pumped into the vessel. The change of the reaction pressure and the percentage of polymer solids in water with time is shown in Figure 1. As can be seen from Figure 1, the pressure of the reactor remains constant until liquefied CTFE is consumed. A sharp pressure drop is then observed corresponding to the consumption of gaseous CTFE. The conversion of monomer to polymer appears to have a linear time dependence, which is consistent with the emulsion polymerization of other monomers such as styrene or vinylchloride.⁴ The rate of polymerization is directly related to the number of particles by the following equation:⁴ $R_p = 10^3 N' n K_p [M] / N_A$, where N' is the concentration of micelles/particles; n is the average number of radicals per micelle/particle; K_p is a rate constant; [M] is the monomer concentration; and N_A is Avogadro's number. If the number of particles is defined in the first 10 min of polymerization and remains



Figure 2 Time dependence of particle diameter and particle number density (particles/L) for a PCTFE/VAC copolymer (latex 1).

constant, the conversion of monomer to polymer would be expected to follow a linear time dependence. The time dependence of particle diameter and particle number is shown in Figure 2. To determine the time-dependent particle diameter and particle number density, samples were withdrawn from the autoclave while it was under pressure. Despite the experimental error involved in sampling the autoclave under pressure, there does not appear to be a change in particle number density from 0.5–5 h. The particle diameter increased from 0.135 to 0.251 microns with time. Because photon correlation spectroscopy showed a narrow monodisperse distribution of particle sizes for all samples withdrawn from the autoclave during the course of the polymerization, this suggests that the particle number is defined very early in the polymerization and no new particles are created. Other PCTFE/VAC polymerizations showed similar results. As a side note, with increasing levels of VAC, lower levels of ferrous sulfate was required to attain robust polymerizations.

A similar experiment was carried out for latex 2, a copolymer containing CTFE and VDF. Despite the experimental error involved in discharging latex from an autoclave under pressure, the time dependence of % polymer solids in water (Fig. 3), particle size, and particle number (Fig. 4), is consistent with the results obtained for the CTFE-VAC copolymer. The conversion of monomer to polymer appears to show a linear time dependence. Particle size distributions were monodisperse, suggesting that no new particles were created after the initial 10-min of polymerization, the time at which the first dispersion



Figure 3 Solids concentration (% polymer in water) as a function of time for a PCTFE/VDF copolymer (latex 2).

sample was withdrawn from the autoclave. Ammonium perfluorinated octanoate was rapidly charged into the autoclave 80 min after the start of polymerization. However, because the particle size distributions of the samples withdrawn from the autoclave before and after the addition of surfactant were monodisperse and narrow, it can be concluded that the surfactant did not induce the creation of new particles when added at this stage of polymerization. For example, dispersion samples withdrawn after 77, 127, and 172 min had particle sizes ranging from 0.12–0.13, 0.14– 0.15, and 0.15-0.17 microns, respectively. As shown by Figure 4, the particle number remained constant after the first 10 min of polymerization, within experimental error, despite the late addition of surfactant.

The first sample from the preparation of latex 2 was withdrawn after 10 min of polymerization. Elemental analysis of the dried polymer contained 20.99% carbon and 0.40% hydrogen. This would correspond to a polymer containing 12.8 wt % VDF. Seven weight percent VDF was initially charged to the autoclave corresponding to a theoretical hydrogen content of 0.22 wt %. However, if it is assumed that all of the *t*-BHP is incorporated into the structure of the polymer, a hydrogen content of 0.71 wt % would be expected. Not knowing the free radical efficiency of radicals deriving from *t*-BHP, it is unknown to what extent t-BHP contributes to the 0.4 wt % hydrogen observed in the polymer. If a 30-40% free radical efficiency is assumed, 0.36–0.41 wt % hydrogen would be expected, assuming that the reactivity ratios of CTFE and VDF are equivalent.

The intrinsic viscosity of dried polymer obtained from the first sample (10 min of polymerization) of latex 2 was 0.23 dL/g corresponding to a molecular weight of 68,118 using the relationship^{1,2} $[\eta] = 6.15 \times 10^{-15} M_n^{0.74}$. The final sample of dried polymer obtained after the polymerization had been terminated, and the dispersion discharged from the autoclave had an intrinsic viscosity of 1.24 dL/g, corresponding to a molecular weight of 656,080. From these measurements it can be seen that low molecular weight species are indeed generated in the initial stages of polymerization, which is consistent with the theory of homogeneous nucleation. Athough the final polymer molecular weight was an order of magnitude higher than the molecular weight obtained after the inital 10 min of polymerization, it was surpising to observe a molecular weight as high as 68,118. This suggests that particle nucleation (micelle formation) might occur over a time period significantly less than 10 min, thus promoting the growth of polymer having somewhat high molar mass at the earliest moments of polymerization.

Latices 3–7 were prepared in a similar fashion, as described in Table I. Although a number of variables were changed in the preparation of each latex, emphasis is placed on the amount of initial redox catalyst charged to the reactor. It was observed in the preparation of latices 1 and 2 (Figs. 2 and 4), that the particle number is defined very early in the polymerization and does not change. In the case of latex 1, the particle number was found to be fixed as early as 30 min into the polymerization. In the case of latex 2, the particle number was found to be fixed as early as 10 min into the polymerization. In the preparation of latex 6, a CTFE–VDF copolymer prepared using no surfactant, a sample was withdrawn after injection of the initial charge of the redox catalysts,



Figure 4 Time dependence of particle diameter and total particle number for a PCTFE/VDF copolymer (latex 2).



Figure 5 Dependence of particle number density (particles/L) on the amount of redox catalyst, SmBS or *t*-BHP, injected over the first 10-min period (latex 3–7).

which took place over a 10-min period. Analysis of this latex by photon correlation spectroscopy revealed a very narrow distribution of particle sizes, ranging from 54 to 86 nm. Analysis of the latex after 6 h revealed a narrow particle size distribution from 212 to 248 nm, suggesting that no new particles were created. This further indicates that the particle number is established in 10 min or less and does not change. It can thus be concluded, that for latex 1, vinylacetate was added after the critical micelle concentration had already been defined, and played no role in defining particle number density.

In a past investigation by other researchers, the surfactant-free polymerization of VDF with hexafluoropropene using ammonium peroxydisulphate as a free radical source, yielded a different result.¹⁶ Using the ammonium peroxydisulphate free radical system, it was claimed that long reaction times were necessary for complete particle nucleation and constant reaction rate. Particle number was shown to increase with time until a given quantity of monomer was consumed. In the best case a particle density of roughly 4.0 imes 10¹⁶/L was obtained. This particle number density is roughly half of that which can be obtained using the SmBS/t-BHP/Fe redox system. Further comparisons of the two surfactant-free emulsion polymerization of fluoroolefins are limited by the lack of experimental details given for the ammonium peroxydisulphate free radical system.

Because the particle number density is defined in less than 10 min, the data is best analyzed by comparison of the particle number density as a function of the amount of initial redox initiator added over the short 10-min time period. Analysis shows that the number of particles generated per liter of water is a linear function of the SmBS or t-BHP (ppm in water) added in the first 10 min (Fig. 5), within this experimental range of initiator concentration. It is not the time over which the initial charge of polymerization initiator is added that is critical, rather the quantity of initiator that is charged during the first minutes of polymerization and the resulting concentration of initiator in the autoclave, which determines the number of micelles formed. As shown in Table I, the increase in particle concentration with the initial charge of redox catalysts seems to be independent of other factors such as the quantity of charged monomer, either CTFE or VDF, or the amount of charged ferrous sulfate heptahydrate. In fact, in the case of latex 7, which had the least amount of the initially charged monomer, the highest particle number density was obtained. However, it must be assumed that a critical minimum level of monomer must be present to obtain a high particle number density. Most importantly, latex 7 shows that a high particle number density can be obtained, which has previously been a shortcoming of surfactant-free polymerization. Because the rate of polymerization is directly proportional to the particle number density, it is very important that the surfactant-free process generate a high particle number density for it to be commercially viable. The particle size distribution of latex 7 is shown in Figure 6. Figure 7 is a representative SEM micrograph of a CTFE/ VDF copolymer latex prepared in a 1000-gallon autoclave using the surfactant-free emulsion process under conditions similar to those described for the preparation of latices 3–7.

Redox Catalyst Stoichiometry

One important aspect of the surfactant-free emulsion process used in this investigation is the ratio



Figure 6 Particle size distribution by photon correlation spectroscopy of a PCTFE/VDF copolymer emulsion using surfactant-free emulsion polymerization (latex 7).

(- 100 nm)



Figure 7 SEM micrograph of PCTFE/VDF surfactant-free emulsion particles prepared in a 1000 G autoclave.

of oxidizing agent to reducing agent. Analysis of the aqueous phase of various P(CTFE/VDF) dispersions by ion chromatography revealed the following concentrations of anions: F⁻ (50 µg/mL), Cl⁻ (70-80 µg/mL), SO₄²⁻ (70 µg/mL), oxalate (0-70 µg/mL), and ClF₂CCO₂⁻ (trace, <1 µg/mL). The oxalate levels are indicative of an excess of oxidizing agent during polymerization, and is a result of the oxidation of the monomers. The SmBS/t-BHP/Fe redox system generates various free radical initiating species and is described by the following equations. Metabisulfite is first converted to bisulfite in water.

$$S_2O_5^{2-} + H_2O \rightarrow 2HSO_3^{-}$$
 (1)

Free radicals are generated by the reaction of bisulfite with *t*-BHP.

$$ROOH + HSO_3^{-} \rightarrow RO \bullet + OH^{-} + HSO_3 \bullet$$
 (2)

Ferrous iron is oxidized in the presence of the hydroperoxide to ferric iron and is regenerated by reaction with bisulfite according to the following equations:

$$ROOH + Fe^{+2} \rightarrow Fe^{+3} + RO \bullet + OH^{-}$$
(3)

$$2 \text{ HSO}_3^- + 2\text{H}_2\text{O} + 4\text{Fe}^{+3} \rightarrow 4\text{Fe}^{+2} + 2\text{SO}_4^{-2} + 6\text{H}^+$$
 (4)

Iron (III) also reacts with bisulfite according to eq. (5):

$$\operatorname{Fe}^{+3} + \operatorname{HSO}_{3}^{-} \rightarrow \operatorname{Fe}^{+2} + \operatorname{HSO}_{3}^{\bullet}$$
 (5)

Because 1 mol of SmBS generates 2 mol of bisulfite, SmBS is charged in a 2:1 molar ratio relative to the *t*-BHP. Three experiments were carried out in which (1) SmBS and t-BHP were charged in a 1.07:1 equivalent ratio (latex 8); (2) SmBS and *t*-BHP were charged in a 0.98:1 equivalent ratio (latex 9), and (3) by alternately charging the SmBS in large excess and then the *t*-BHP in large excess such that overall the stoichiometry was maintained but at any given time, one of the redox species was in large excess relative to the other (latex 10). As shown in Table II, when the SmBS is present in excess almost undetectable levels of oxalate are present. If the oxidizing agent is present only in slight excess, then low levels of oxalate are present. In the case of latex 10, where the SmBS was initially in large excess, then the *t*-BHP was in large excess, the highest levels of oxalate are present. This is also reflected in the polymerization times. However, in each case high levels of polymer solids in water can be obtained in the absence of surfactants or ionic comonomers.

The role of iron demands further clarification. It is well known that iron is readily oxidized and reduced between Fe(II) and Fe(III) in a one electron transfer. In the absence of iron, polymerizations are sluggish, sometimes taking days, depending on other factors. This suggests that reactions I and II are not significant. Thus, it can be tentatively concluded that reactions III and V are the dominant free radical pathways.

Postadded Fluorosurfactant

Although very high levels of polymer can be dispersed in water in the absence of surfactant, in some instances it is desirable to postadd surfactant to further tailor particle size and distribution. Postadded surfactant is defined as surfactant that is added to the autoclave after stable primary emulsion particles have been created in the absence of surfactant. Postadded surfactant either absorbs onto the surface of existing particles or creates new particles. If the primary particles are present in sufficient quantity, and combined they have sufficiently large surface area, the postadded surfactant will absorb onto the surface of the existing particles; thus, no new particles are created. Although postadded surfactant will improve latex stability, it will not have a role in defining latex particle size or distribution. If surfactant is added very early after the primary particles are created, that is, before they have reached sufficient surface area to absorb all of the surfactant, secondary particles will be created. A series of four latices were prepared in which a fluorosurfactant, the lithium salt of perfluorinated octane sulfonic acid, was postadded to the dispersion after the creation of primary particles took place in the absence of surfactant. In each case, postadded surfactant was charged at some point during the charging of the continuous feeds of redox initiator: (latex 11) 102 min after the initial charging of polymerization initiators, rapid addition; (latex 12) 17 min, 4 min addition time; (latex 13) 1 min, surfactant was pumped over a 7-min period; (latex 14) 2 min, rapid 1 min addition.

As shown in Table III, (latex 11) the addition of surfactant 102 min after the charging of the initial charge of redox initiator was the least effective in manipulating particle size and distribution. The particle size distribution obtained is as narrow as latices 3-7 in which no surfactant was used. Despite the high level of fluorosurfactant charged, no new particles were generated when fluorosurfactant was added at this late stage of polymerization. This is consistent with the results obtained for latex 2. In the preparation of latex 12, fluorosurfactant was added 17 min after the complete addition of the initial charges of redox initiators, which was effective in creating a second distribution of particles, though the wt % of the second generation of particles was only 31%. This demonstrates that the surfactant-free method is a powerful tool in the creation of primary particles even when compared to fluorosurfactant used in a 0.5 wt % concentration. As demonstrated by latex 13, if surfactant is charged immediately after the initial charging of redox initiators, but at a slow rate over a period of 7 min, a broad particle size distribution is obtained.

When fluorosurfactant was added rapidly (latex 14, Fig. 8) and immediately after addition of the initial charge of polymerization initiator, a bimodal distribution is obtained having the smallest overall particle sizes. If a surfactant is to be used to further manipulate particle size and distribution, it must be charged immediately after the surfactant-free creation of the primary particles. At low levels of surfactant, all things being equal, the highest particle density, and the smallest particles are obtained when the surfactant is added before the primary particles have a chance to grow in size and increase their surface area, such that secondary particle formation favorably competes with surfactant absorption onto



Figure 8 Particle size distribution by photon correlation spectroscopy of a PCTFE/VDF copolymer prepared by rapidly postadding lithium perfluorooctyl sulfonate immediately after the creation of primary particles in the absence of surfactant (latex 14).

existing particles. Similar results are obtained using perfluorinated ammonium octanoate.

Conventional Emulsion Polymerization of Fluoroolefins

One objective of the present investigation was to compare conventional emulsion polymerization typically practiced by fluoropolymer dispersion producers to the surfactant-free process described in this investigation. Latex 15 was prepared using ammonium perfluorooctonoate, a preferred surfactant used in the preparation of fluoropolymers, which was precharged to the initial batch of deionized water, a practice standard in the industry.¹⁷⁻²¹ The polymerization was carried out thereafter in a similar fashion to the emulsions prepared by the surfactant-free process. An initial charge of redox initiators was followed by a continuous charge of redox initiators in the usual fashion. Photon correlation analysis of the resulting narrow particle size distribution showed a range of particles from 0.22-0.25 microns (dw = 0.232 microns; dn = 0.232 microns, where dn is the number-average distribution, and particle number = 4.89×10^{16} , or 2.33×10^{16} particles/L). This experiment demonstrates that the use of conventional emulsification methods, wherein fluorosurfactant is precharged to an autoclave prior to the onset of polymerization in order to emulsify the developing polymer mass, results in a lower particle number density than all of the latices prepared by the surfactant-free method described in this investigation. When roughly an equivalent amount of fluorosurfactant is postadded to primary particles created in the absence of surfactant (latex 14, particle number = 1.34imes 10¹⁷ particles/L), a dispersion is obtained having almost an order of magnitude higher particle number density than latices prepared using precharged unbound emulsifier. This suggests that *in situ*-created bound emulsifying ionic species is more effective than the prepolymerization addition of 100-2000 ppm of a fugitive fluorosurfactant.

Disuccinic Acid Peroxide/t-BHP/SmBS/Fe Initiator System

Using the surfactant-free emulsion process at 45°C, 40-45% polymer solids in water is typically achieved. Increased levels of self-emulsifying fluoropolymer in water is foreseeable with further optimization. Without further optimization, higher polymer solids have been obtained by the addition of disuccinic acid peroxide to the existing redox initiator system. When used in the temperature range from 40-45°C, succinic acid peroxide does not decompose into free radicals. In the manufacture of fluoropolymers, it is typically used above 90°C to impart carboxylic acid functionality onto the emulsified particle in order to improve latex stability.²²⁻²⁴ However, decomposition of succinic acid peroxide at lower temperatures can be induced by attack of an alkyl free radical, yielding an ester and an acyloxy free radical. At 45°C it is most likely that succinic acid peroxide is either induced to decompose into a carboxylic acid-terminated acyloxy free radical (HO₂CCH₂CH₂CO₂·), or it is involved in chain transfer reactions yielding other carboxylic acid containing free radical species. Regardless of the mechanism, which was not the focus of this investigation, increased polymer solids emulsified in water was obtained. Latex 16 was prepared by the slow addition of succinic acid peroxide during the continuous addition of redox initiator. Without undue optimization, 48% polymer solids in water was obtained, using a surfactant-free emulsion process and 660 ppm of succinic acid peroxide (based on polymer solids).

Latex Purification and Surface Charge Evaluation

To better understand the amount of charged species bound to the self-emulsifying fluoropolymers, a series of latices were prepared at various temperatures (Table IV). The aqueous phases of the latices were purified by techniques well known in the literature,²⁵ as described in the experimental section for latices 17–19. The dispersions were treated with an excess of sulfonated polystyrene ion-exchange resin, the hydrogen form, to remove cations. Because of the strong sulfonic acid groups bound to the surface of the fluoropolymer particles that compete for cations, an excess of strong acid ion exchange resin is required. The ion-exchanged latex was then poured into a cellulose ester dialysis membrane, which was placed in a deionized water reservoir. The reservoir was replaced daily with fresh deionized water until a constant 1-day conductivity measurement was obtained corresponding to deionized water. The unpurified latex contained in addition to $SO_{4^{-2}}$ and oxalate anions (Table II), 70-80 μ g/mL of Cl^- and 50–125 µg/mL of F^- . The following is a list of typical metal concentrations (μ g/mL): Si, 99.7 (typical impurity when using a glass lined autoclave); Na, 155; and Fe, 12-30, obtained using AAS and ICP. To assure that the aqueous phase of the latices was sufficiently purified by the combination of ion exchange and dialysis, samples of the latices were reanalyzed by AAS and ICP. Concentrations of anions and metals for purified latex 18 were as follows (ppm): F^- , 0.8; Cl^{-} , 1.1; SO_{4}^{-2} , 1.4; Fe, 0.2; Na, 8.2; and Si, nondetectable, <0.1. Because the AAS and ICP measurements were conducted after ashing the latex (polymer plus aqueous phase), it can be concluded that little if any metal salts are encapsulated in the interior of the fluoropolymer particle. The purified latices were then titrated with a 0.05% solution of NaOH in water to calculate the NaOH equivalents of sulfonic acid-terminated self-emulsifying fluoropolymer. As polymerized, the latices typically have a pH from 1.75 to 2.5. If unpurified latex is titrated, three end points are identified corresponding to a strong acid, a medium strength acid, and a weak acid. After purification, only a single end point is observed, corresponding to that of a strong acid.

As shown in Table IV, the highest levels of sulfonic acid-terminated fluoropolymer are obtained when the polymerization is carried out at elevated temperatures (latex 19). Although 0.011 NaOH molar equivalents/kg of polymer corresponds to very low levels of sulfonic acid bound to the surface of the fluoropolymer particles, it should be emphasized that fluorosurfactants are very strong surface active agents, being effective at concentrations below 0.01%. Due to the inductive effect of fluorine, perfluorinated alkyl sulfonic acids are very strong acids, being completely disassociated in water.²⁶ For the latices prepared between 25–45°C, significantly lower levels of bound sulfonic acid are observed. This is probably related to the reduced solubility of CTFE in water at this temperature. Latex 17, prepared with a significantly higher level of VDF, had the highest level of sulfonic acid when prepared from $40-45^{\circ}$ C. This can be attributed to the greater solubility of VDF in the aqueous phase, which would be expected to lead to a higher initiator efficiency. Because VDF has a solubility of 6.3 cm³/0.1 kg water at 25°C (1 atm),²⁷ compared to CTFE, which is practically insoluble in water, it is likely that the predominant mechanism for chain initiation is the attack by free radicals on VDF in the aqueous phase.

Latices 20 and 21 yielded surprising results. Because the polymerizations were conducted at room temperature, the lowest temperature investigated, they might be expected to contain the lowest level of bound sulfonic acid. However, because the terpolymerizations were conducted using from 3.7-5.1 wt % of water-soluble vinylester, it was anticipated that a higher initiator efficiency would be observed, resulting in a higher level of bound sulfonic acid. Contrary to expectations, the presence of a water-soluble monomer using water-soluble free radical initiators did not appear to significantly impact the level of bound sulfonic acid. It is difficult to draw solid conclusions because (1) it is not known to what extent vinylester-rich free radical containing oligomers formed in the aqueous phase combine and are removed during latex purification; and (2) the propensity of vinylester-rich oligomers to absorb onto the fluoropolymer particle is not understood. In contrast, fluorinated ionic oligomers would be expected to readily absorb onto the surface of a fluoropolymer particle when a sufficient chain length is obtained.

Bisulfite Radical Efficiency

The initiator efficiency of SmBS for latex 19 was determined by dividing the calculated NaOH equivalents of sulfonic acid terminated fluoropolymer/kg of polymer obtained (Table IV) by the molar equivalents of charged SmBS. A 30.7% bisulfite free radical efficiency is obtained. This crude calculation ignores any loss of low molecular weight sulfonic acid-terminated fluorinated oligomers that might be lost during latex purification. Because 28% of the total SmBS injected was rapidly charged to the autoclave during the 10-min initial charge of redox catalysts, a process that generates predominantly low molecular weight ionic species, it is assumed that the calculated bisulfite free radical efficiency is at least 30.7%, but is probably understated.

CONCLUSIONS

The surfactant-free emulsion polymerization of copolymers containing CTFE using redox free radical initiators, t-BHP/SmBS/Fe, is a versatile, robust method for obtaining surfactant-free fluoropolymer emulsions. Particle number density can be directly related to the quantity of initially charged redox catalysts, over the concentrations studied. Sulfonic acid surface charge can be readily quantified. To elucidate the dominant free radical initiating species, (1) an understanding of the free radical efficiency of t-BHP would be required, and (2) low molecular weight ionic species would have to be more thoroughly characterized. These polymerizations are complicated by the fact that the initiating species are present in ppm levels, and are bound to intractable fluoropolymers. However, the surfactant-free process, when optimized, and combined with the postaddition of fluorosurfactants or disuccinic acid peroxide, yields fast conversion rates, high particle number density, excellent latex stability, and high levels of emulsified solids in water.

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