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In-Situ Investigation on the Mechanism of Dispersion Polymerization in Supercritical Carbon Dioxide

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ABSTRACT: The effect of stabilizers on the particle formation stage in dispersion polymerization of methyl methacrylate in supercritical CO_2 has been studied by in-situ turbidimetry. The average particle diameter (250 nm) and particle number density are similar at the end of this formation stage for the stabilizers poly(dimethylsiloxane)-*b*-poly(methyl methacrylate-*co*-methacrylic acid) (PDMS-*b*-P(MMA-*co*-MA)) and poly(1,1-dihydroperfluorooctyl acrylate)-*b*-polystyrene (PFOA-*b*-PS). Particle diameters are only about twice as large for perfluoropolyether acid (PFPE-COOH) but become much larger for grafted PDMS−monomethacrylate due to less effective surface coverage. The final particle number density changes little for conversions from 1% to completion for PDMS-*b*-P(MMA-*co*-MA) but increases for PFOA-*b*-PS due to formation of new particles in block copolymer micelles.

Introduction

Recently, fluorocarbon- and siloxane-based homopolymers, macromonomers, and copolymers have been employed successfully as stabilizers in dispersion polymerization of methyl methacrylate (MMA), styrene, and other soluble monomers in CO_2[1−5] as reviewed elsewhere.[6] An important goal is to understand how the final particle morphology, molecular weight, and conversion are related to the surfactant architecture and concentration and the solvent quality, which is closely related to solvent density. Steric stabilization is particularly challenging in CO_2 due to its weak van der Waals forces and thus weak solvent strength.

The mechanism of surfactant stabilization is considered to be more complex and less well-understood in dispersion polymerization than emulsion polymerization.[7] In dispersion polymerization in liquid solvents, the nucleation stage is completed very rapidly, typically at a conversion below 0.1%,[2,8−10] as described by Paine's model.[11] In CO_2, the mechanism of dispersion polymerization has recently been investigated in-situ for PMMA[12] and poly(vinyl acetate).[5] Coagulative nucleation and controlled coagulation regions have been identified. In the controlled coagulation region, the surface area of the dispersion grows too fast for complete coverage of the surface by surfactant. Near the end of the controlled coagulation region, which can last tens of minutes, the surfactant covers the particle surface fully, preventing further coagulation. At this point, the particle number density approaches the final value as has also been seen in organic solvent.[7]

It is difficult to follow the particle formation during the initial stage of dispersion polymerization with either electron microscopy[2] or dynamic light scattering (DLS).[9,10] Recovery of particles by depressurization can introduce artifacts into SEM micrographs, since the solvent-laden particles may agglomerate. This problem is compounded by plasticization of the particles by CO_2, which can make them sticky.[13] In addition, the residual monomer can dissolve the nucleated particles. DLS measurements have been limited to the first 3−5 min beyond phase separation, after which multiple scattering began to affect the measurements.[9,10] Turbidimetry can be used to analyze much more concentrated emulsions and with more rapid data acquisition. The particle size and number density are determined from Mie scattering theory.[14,15]

For acrylate emulsions stabilized by poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) in CO_2,[16] it was observed by turbidimetry that the emulsion flocculates as the density is lowered. This "critical flocculation density" is located close to the point where the upper critical solution density where PFOA phase separates from CO_2 in bulk solution. This experimental observation is in agreement with lattice-fluid self-consistent-field theory[17,18] and Monte Carlo computer simulation.[19]

Only two previous studies have explored dispersion polymerization in-situ in CO_2, both with turbidimetry.[5,12] In a study of polymerization of MMA, PDMS-monomethacrylate (PDMS-mMA) macromonomer was grafted to the particles chemically via copolymerization.[12] The rapid formation of 1−2 μm particles after ~35 min indicated insufficient grafting of stabilizer at the surface of the particles, even with 14% PDMS/MMA (w/w). In the polymerization of vinyl acetate with a variety of PDMS- and PFOA-based block copolymers, the particle diameter reached 2−3 μm after only 10−40 min. In CO_2, it would be desirable to form particles smaller than 200 nm to produce highly stable latexes. The settling rate is rapid due to the low density and viscosity of CO_2 relative to water. A better understanding of the particle formation stage is needed to design strategies for producing very small particles.

Our objective is to study the mechanism of MMA polymerization in-situ by turbidimetry in order to produce particles on the order of 250 nm in diameter during the particle formation regime. The polymerizations are examined as a function of stabilizer type, stabilizer and monomer concentration, pressure, and cosolvent addition. The stabilizers include a commercial perfluoropolyether acid (PFPE-COOH), which has been

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used recently to produce 2.5 μm PMMA particles,[20] poly(1,1-dihydroperfluorooctyl acrylate)-*b*-polystyrene (PFOA-*b*-PS) which has been used in styrene polymerization,[21] and poly(dimethylsiloxane)-*b*-poly(methyl methacrylate-*co*-methacrylic acid) (PDMS-*b*-P(MMA-*co*-MA)) which has been used to produce 700 nm PMMA particles by dispersion polymerization in CO_2.[22] The surfactant PDMS-*b*-P(MMA-*co*-MA) has an “ambidextrous” nature in that it stabilizes PMMA latexes in CO_2 and in water due to ionization of methacrylic acid.[22] The multiple anchor segments in the PDMS- and PFOA-based copolymers, styrene or MMA, adsorb to the PMMA surface. For PFPE-COOH, only the single COOH group adsorbs to PMMA as shown by FTIR spectroscopy.[20] We will examine how the difference in stabilizer adsorption, along with the difference in the solvation and molecular weight of the CO_2-philic segments of these surfactants, influences the particle formation. Another important objective is to determine at what point the particle number density becomes equivalent to the final particle number density.

Experimental Section

Materials. Methyl methacrylate and 2,2′-azobis(isobutyronitrile) (AIBN) were obtained from Aldrich and purified as described previously.[23] PFPE-COOH with an average molecular weight of 2500 was used as received (DuPont Krytox 157FSL). PFOA-*b*-PS (M_n: 27 000-*b*-3700), a gift from J. DeSimone, was synthesized by using the “iniferter” technique.[24,25] PDMS-*b*-P(MMA-*co*-MA) (M_n: 5000-*b*-(1100-*co*-500)) was synthesized previously.[22] Carbon dioxide (Praxair instrument grade, 99.99%, <15 ppm of oxygen) was used without further purification.

Turbidity Measurements. Turbidity spectra were obtained in-situ during the first 2 h of polymerization in supercritical CO_2 with a specially designed high-pressure apparatus which has been described in detail.[5,26] The path lengths of the optical cells were 1.00 and 0.29 mm. The turbidity measurements were conducted by scanning from 560 to 760 nm every 1−2 min after phase separation with a Beckman DU-40 spectrometer.[5,12] Phase separation was defined as the point where an orange tint was observed, which indicated Rayleigh scattering by small particles of nucleated polymer.

The turbidity τ is defined as

$$\tau = (1/L)\ln(I_0/I) \tag{1}$$

where L is the path length in centimeters; I_0 and I are the intensities of the incident and transmitted light, respectively. For a monodisperse system of nonabsorbing isotropic spheres in the absence of multiple scattering the turbidity is given by Kourti[27]

$$\tau = 3\phi K/2D \tag{2}$$

where ϕ is the volume fraction of the dispersed phase, D is the particle diameter, and K is the scattering coefficient, which is a complex function of two dimensionless parameters: m, the ratio of the refractive index of the dispersed to continuous phase, and α equal to $\pi D/\lambda$ (where λ is the wavelength of the incident light).[14,28] Given α and m, K is calculated by using the Mie theory.[29]

From eq 2 the ratio of turbidities at two different wavelengths is given by eq 3.

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

The particle diameter may be determined with eq 3 with an iterative procedure. Given D, the volume fraction of the dispersed phase and the particle number density may be calculated from eq 2. To determine an effective average particle diameter, the latex was assumed to be monodisperse.

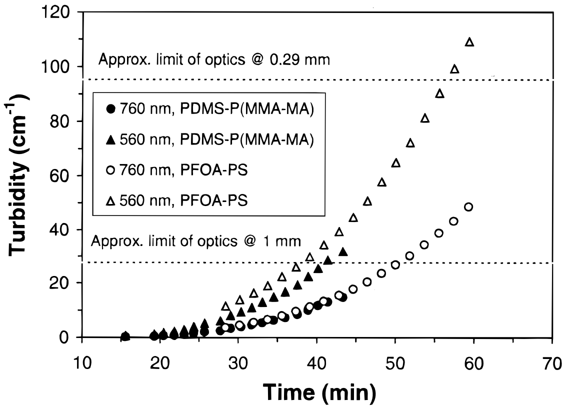

Figure 1. Turbidity at 760 and 560 nm versus time for stabilizer PFOA-*b*-PS with 0.29 mm path length and PDMS-*b*-P(MMA-*co*-MA) with 1.00 mm path length.

Table 1. Refractive Indices of Continuous and Dispersed Phases[a]

pressure (bar)	n_{cont}	n_{dis}
207	1.21	1.43
276	1.23	1.41
345	1.24	1.40

[a] Cited from O’Neill[12] with 20% MMA/CO_2 (w/w).

All the reactions were conducted at 65 °C and initiated by 1% AIBN/MMA (w/w). The particle size and number density at high conversions were determined from analysis of the recovered dry powder with a Joel JSM-35C scanning electron microscope (SEM).

Results and Discussion

Effect of the Stabilizer Structure. Two types of block copolymers PFOA-*b*-PS and PDMS-*b*-P(MMA-*co*-MA) were employed as stabilizers in the polymerizations. Figure 1 shows the measured turbidities at 560 and 760 nm with two different path lengths of 0.29 mm for PFOA-*b*-PS and 1.00 mm for PDMS-*b*-P(MMA-*co*-MA) at 276 bar, with 20% MMA/ CO_2 (w/w) and 5% stabilizer/MMA (w/w). The dashed lines represent the optical density limit due to multiple scattering for the two cells. This limit is defined for an absorbance of 1.2.[26] Data collected above this limit were not used due to large deviations from linearity in τ vs ϕ. More turbid dispersions could be measured (longer polymerization times) with the shorter path length cell. The accuracy of turbidity at both wavelengths was evaluated as 0.5%.[12]

Refractive indices for the continuous and dispersed phases of the latex were taken from Table 1 in O’Neill et al.[12] The estimated uncertainties in the continuous phase and the PMMA dispersed phase refractive indices were ±0.01 and ±0.02, respectively. No corrections were made for the dependence of refractive indices on wavelength.[30] The average particle size and particle number density were calculated as shown in Figure 2a,b for polymerization with the above two block copolymers, PFPE-COOH and PDMS-mMA, and with no stabilizer. Uncertainties in the measured turbidities contributed the majority of the error in particle size at low turbidities, while at higher turbidities uncertainties in the refractive indices of the dispersed phase (due to uncertainties in the phase composition) became the major contributor. The uncertainty in diameter was found to

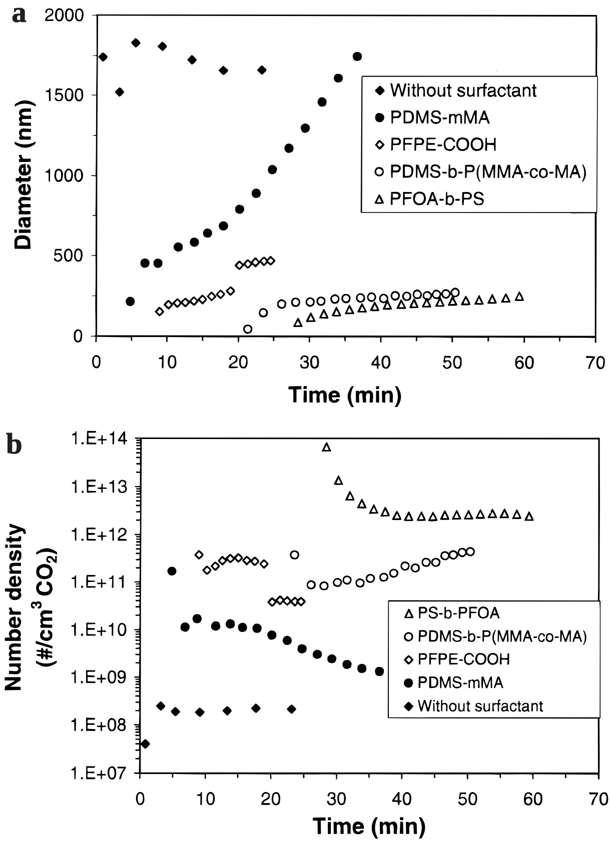

Figure 2. Dispersion polymerization of MMA in CO_2 at 65 °C and 276 bar with 20% MMA/CO_2 (w/w) and 5% stabilizer/MMA (w/w): (a) average particle size and (b) particle number density. The case without stabilizer is shown for comparison.

be approximately ±20% for all measurements.[30] This uncertainty in particle size measurement is acceptable for the comparison of latexes formed by different stabilizers, because the refractive index ratio will be similar for all latexes. In the absence of stabilizer, collisions of the newly formed nuclei led to coagulation and settling of large particles within a few minutes. With the addition of a block copolymer stabilizer, the particle sizes were smaller than 300 nm. The stabilizers delayed the phase separation by controlling coagulation of the nuclei. Notice in Figure 2b that the number density decreased rapidly and then leveled out. Because of this controlled coagulation, the addition of stabilizer increased the particle number density by 3−4 orders of magnitude. The plateaus for the polymerizations with block copolymer stabilizers shown in Figure 2a,b indicate the end of the controlled coagulation region. At this point enough stabilizer adsorbed at the interface to prevent further coagulation.

In comparison, stabilization by grafting PDMS-mMA macromonomer ($M_n \sim 10\,000$)[26] was much less effective, as indicated by particle sizes an order of magnitude larger and much smaller particle number densities as shown in Figure 2a,b. Apparently, the grafting of the PDMS chains to the surface by chain transfer during the particle formation regime led to lower surface coverage than in the case of the adsorbed block copolymers. The particles coagulate when the area stabilized by the PDMS chains is less than the area of the dispersion produced by polymerization.[11,12]

For dispersion polymerization with grafted stabilizers, Paine developed a semiquantitative model to predict particle size and number density. A critical size, d_{crit}, was defined as the point where the graft available equals the surface area of the growing particles. If grafting occurs by chain transfer to stabilizer, the critical size is

$$d_{crit} = \frac{6[M]MW_M Q_{min}}{\rho C_S [S] N_A} \tag{4}$$

where [M] and [S] are the monomer and stabilizer concentrations, respectively, MW_M and ρ are the molar weight and density of monomer, Q_{min} is the minimum coverage by graft required to stabilize the surface of the particles, C_S is chain-transfer constant for transfer to stabilizer, and N_A is Avogadro's number. At this diameter, represented by the plateau in Figure 2a, the number density of the particles remains essentially constant as coagulation is prevented. With 5.5% PDMS-mMA, O'Neill[12] observed d_{crit} of PMMA by turbidimetry is about 500 nm.

For the present case with adsorption of copolymer stabilizers rather than grafting, the adsorption in mol/cm^2, Γ, may be used to replace C_S[S] in eq 4. From the observation of smaller particles (d_{crit}) formed with the block copolymer stabilizers compared with PDMS-mMA, Γ may be expected to be larger than C_S[S], indicating a higher surface coverage.

The anchor-soluble balance (ASB) of a copolymer stabilizer is known to be a key factor for in controlling adsorption and thus steric stabilization.[8,31] Recently, it has been studied in supercritical fluids by experiment[5] and theory.[32] The soluble block must be long enough to provide steric stabilization, while the anchor block must balance the soluble block properly to achieve adsorption at the particle surface. The COOH group in PFPE-COOH adsorbs on PMMA as shown by FTIR spectroscopy.[20] For this low molecular weight PFPE tail, the radius of gyration is only 1.0 nm in a good solvent.[33] For PDMS-mMA, the radius of gyration is estimated as 2.7 nm.[34] However, PFPE-COOH stabilized 10 times more particles than PDMS-mMA during the particle formation stage. This result is likely due to a higher surface coverage for PFPE-COOH, since both PFPE and PDMS tails are solvated effectively by CO_2−monomer mixtures and may be expected to extend outward into the solvent.[35,36]

For PFPE-COOH, the particles flocculated quickly after about 25 min reaction. The average particle diameter is larger than those produced with PFOA-*b*-PS and PDMS-*b*-P(MMA-*co*-MA). It is likely that the adsorption of PFPE-COOH is weaker than that of the two block copolymers due to only a single CO_2-phobic group, −COOH. As the particles grew, the surfactant was not able to cover all of the surface area. After about 1 h reaction, the product started to settle even with stirring on.

PFOA-*b*-PS contains highly CO_2-soluble block PFOA with a radius of gyration in bulk CO_2 of 1.6 nm.[37] In contrast, R_g is estimated as 2.0 nm for the PDMS block in PDMS-*b*-P(MMA-*co*-MA) at 65 ± 5 °C and the θ pressure[34] (Table 2). The larger length for PDMS is due to the lower monomer molecular weight and lack of long side chains. The PDMS block provides nearly as good stabilization as PFOA as reflected in the particle size and number density in the particle formation stage. Both surfactants have a desirable anchor-soluble balance (ASB) for strong adsorption on the basis of the small particles in Figure 2a.

Table 2. Radius of Gyration of the "CO_2-philic" Segment of the Stabilizer and the Solubility of the Stabilizer in CO_2

stabilizer	M_n (g/mol)	R_g (nm)	solubility (%) (w/w)
PDMS-mMA	10 000	2.7[a]	2.8
PFPE-COOH	2500	1.1[b]	≫5
PFOA-*b*-PS	27 000-*b*-3700	1.6[c]	10
PDMS-*b*-P(MMA-*co*-MA)	5000-*b*-(1100-*co*-500)	2.0[a]	<2

[a] Estimated with $R_g(\theta) = 0.267M_w^{1/2}$.[34] [b] Estimated with $10^3\langle r^2\rangle_0/M = 2.57$.[33] [c] Estimated by Harrison et al.[37]

The stabilities of the final latexes in CO_2 were quite different for the two copolymer stabilizers. Without stirring, latexes stabilized by PFOA-*b*-PS were very stable, whereas those stabilized by PDMS-*b*-P(MMA-*co*-MA) settled rapidly. Without monomer, the solvent quality of CO_2 by itself was insufficient to stabilize the PDMS chains at 65 °C and a pressure well below the theta pressure P_θ (520 bar).[34] The particles were loosely flocculated and could be redispersed with stirring.

Comparison of the in-Situ Measurements with SEM Characterization. The reaction with 20% MMA/CO_2 (w/w) and 5% stabilizer/MMA (w/w) at 65 °C and 276 bar was stopped at 6 h. CO_2 and the residual monomer were vented, and dry product was collected. Scanning electron microscopy was used to characterize the final product. The average particle sizes and number densities were calculated from the micrographs (Figure 3) and compared with the results of in-situ measurement (Table 3). For the slightly agglomerated samples in Figure 3c,d, the uncertainty in number density was 25%. With block copolymer stabilizers, the product was free-flowing powder without agglomeration, and the particles grew larger by hundreds of nanometers after the formation stage. For experiments with PDMS-*b*-P(MMA-*co*-MA), the particle number density increased very little from 50 min to 6 h, indicating that it was essentially fixed during the particle formation stage. During the growth stage after 50 min, particle coalescence appeared to be minimal, indicating efficient stabilization by the stabilizer. The stable particles grow through monomer and oligomer capture but not coagulation. This type of behavior has been observed during dispersion polymerization in liquid solvents.[8,9,11,26] The agreement between the particle number density measured by turbidimetry and SEM suggests the reliability of the turbidimetry measurements. The SEM samples were obtained at high conversions where the particles were relatively monomer free and were thus not prone to agglomerate.

The polydispersity of the final product was much larger for the experiment with PFOA-*b*-PS than that with PDMS-*b*-P(MMA-*co*-MA). Furthermore, the particle number density increased during the growth stage for PFOA-*b*-PS, whereas it changed little for PDMS-*b*-P(MMA-*co*-MA). The very small particles produced with PFOA-*b*-PS must have been formed well after the first 50 min particle formation stage; otherwise, they would have grown to be considerably larger. Perfluoro-based polymeric stabilizers have been demonstrated to form micelles in bulk CO_2.[38,39] These micelles could capture and stabilize growing polymer chains late in the reaction, and thus continuous nucleation occurred through the reaction process. Also, the repulsive interactions between PFOA tails in micelles swollen by PMMA and PFOA tails on PMMA latex particles could inhibit heterocoagulation, that is, capture of swollen micelles or small latex particles by large latex particles. The ability of PDMS-*b*-P(MMA-*co*-MA) to form micelles in CO_2 is unknown. It may be expected that heterocoagulation may be more prevalent for PMMA coated by PDMS versus PFOA, since it is easier for PMMA to pass through a PDMS layer than a PFOA layer on the basis of thermodynamic interactions.[40] PMMA interacts more strongly with PDMS than PFOA, as the surface tension of PMMA is much closer to that of PDMS.[16]

The product stabilized with PFPE-COOH settled down on the bottom of the reactor and was agglomerated but was easily broken up into a free-flowing powder. The SEM (Figure 3c) showed the final average particle diameter was 2.25 μm with a narrow size distribution (Table 3). The ability to stabilize such small particles with a commercially available surfactant is of practical interest. The particle number density decreased from the particle formation stage to the end of the reaction, due to coagulation, indicating incomplete surface coverage as the surface area increased (Table 3). Figure 3d showed the particles produced with PDMS-mMA were partially coagulated.

Effects of Pressure. The density and thus the solvent strength of supercritical CO_2 can be tuned significantly by varying pressure.[41,42] As shown by Monte Carlo computer simulation for a polymer composed of freely jointed segments, the coil−globule transition of a single chain occurs at the same density as the upper critical solution density where the chains phase separate from the solvent.[43] Furthermore, according to theory, this density is also the point where two surfaces with grafted chains flocculate.[32] In the simulations, each segment has the same energy and size as the solvent.

Figure 4a,b shows the effect of pressure on the polymerization with PDMS-*b*-P(MMA-*co*-MA). At 345 bar, the particles are modestly smaller relative to 276 bar. The nuclei grew to 200 nm in less than 30 min. At 207 bar, this growth took place in only 5 min. Here PMMA is much less soluble and precipitates sooner. The particles did not settle and would not settle even without stirring. However, according to the plateau regions in Figure 4a,b, the particle diameters and number densities are in the same range for all three pressures. The reduction in solvent quality with pressure produces two effects on the stabilizer. The PDMS tails are less extended providing weaker stabilization, while the driving force for adsorption onto PMMA increases.[32] The similar results for particle formation at all three pressures suggest that there may be some cancelation between these two competing effects. In contrast, the final product morphologies were quite different. At the two higher pressures, a freely flowing powder was collected after 6 h reaction with a conversion of over 90%. These nonflocculated particles were relatively monodisperse with an average diameter of about 700 nm. At 207 bar, large agglomerates were formed with a yield of less than 50%. In the particle formation stage, particle coagulation was controlled by the large amount of monomer which acted as a cosolvent. At high conversions where the cosolvent concentration was small, the PDMS chains partially collapsed, leading to flocculation and agglomeration.

Effect of Stabilizer Concentration. An increase in the stabilizer concentration may be expected to produce smaller particles with a higher particle number density.[7]

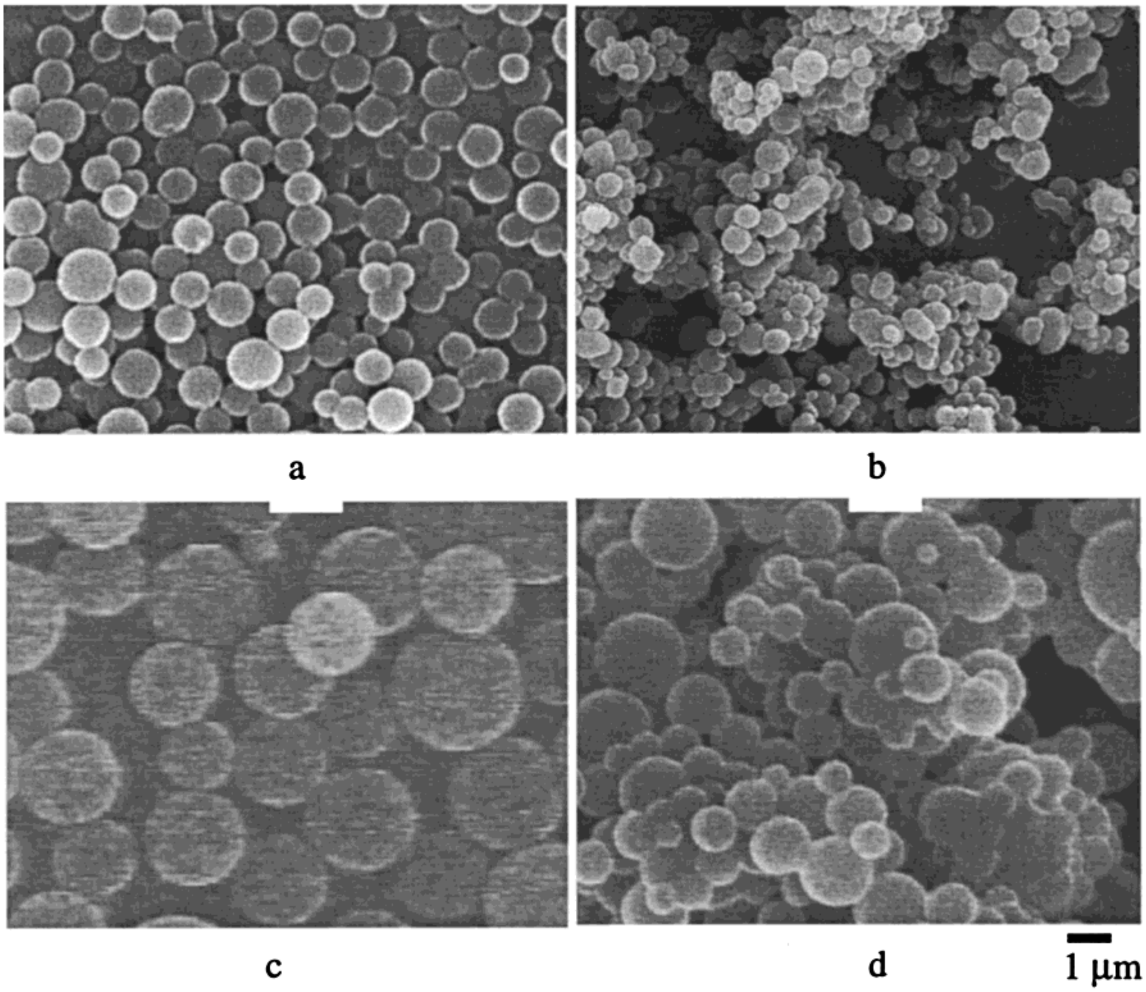

Figure 3. Scanning electron micrographs for dispersion polymerization of MMA in CO_2 at 65 °C and 276 bar with 20% MMA, 5% stabilizer after 6 h reaction: (a) PDMS-*b*-P(MMA-*co*-MA); (b) PFOA-*b*-PS; (c) PFPE-COOH; (d) PDMS-mMA. The bar represents 1 μm.

Table 3. Characterization of Particles Formed at 50 min (Turbidimetry) and at 6 h (SEM) with 20% MMA/CO_2 (w/w), 5% Stabilizer/MMA (w/w), and 1% AIBN/MMA (w/w) at 65 °C and 276 bar

		D_n (nm)		no. density (no./cm^3 of CO_2)		D_w/D_n
stabilizer	yield (%)	50 min	6 h	50 min	6 h	6 h
PDMS-mMA	93	1700[a]	N/A	1.4×10^9 [a]	N/A	1.31
PFPE-COOH	72	470[a]	2247	3.8×10^{10} [a]	9.5×10^9	1.06
PFOA-*b*-PS	97	250	357	2.6×10^{12}	5.3×10^{12}	1.55
PDMS-*b*-P(MMA-*co*-MA)	98	260	770	4.0×10^{11}	5.3×10^{11}	1.04

[a] 25 min reaction.

In MMA polymerization in CO_2, large changes in particle size and number density were observed in the particle formation stage as PDMS-mMA macromonomer concentration was raised from 0.92 to 14%.[12] In contrast, Figure 5 illustrates that the particle size varies little as the stabilizer concentration is varied from 0.6 to 5.4%. For 0.6% PDMS-*b*-P(MMA-*co*-MA) and 20% monomer in CO_2, after 40 min ~250 nm particles are formed with a number density of 8×10^{11}/cm^3 of CO_2. Assuming all the stabilizer molecules are adsorbed on the particle surface, the maximum surface coverage was estimated as 2 nm^2/per stabilizer molecule, but the actual area may be significantly larger. In comparison, a value of 11−13 nm^2 was determined for PMMA particles in hexane stabilized by 5% PDMS-*b*-PS.[31] Thus, the observation of small particles in Figure 5 for 0.6% stabilizer is reasonable. The small differences in the particle diameters for the four stabilizer concentrations may be due to small differences in initiator concentration and uncertainties in the turbidity measurements. However, particles with 0.6% stabilizer were highly agglomerated after 6 h, and the conversion was less than 50%. For the higher stabilizer concentrations, the products were collected as freely flowing powder with more than 90% conversion. For 0.6% stabilizer, the increase in the surface area in the growth stage beyond 40 min appears to overwhelm the ability of the dilute stabilizer to provide full surface coverage. With bare exposed surfaces, substantial coagulation takes place. In the agglomerates, termination becomes more prevalent as the ability of monomer to diffuse into the growing chains is diminished.[26,44] For the higher stabilizer concentrations, the particles do not agglomerate, resulting in less termination and higher conversions.

Effects of Monomer Concentration and Cosolvent. The monomer concentration was varied for poly-

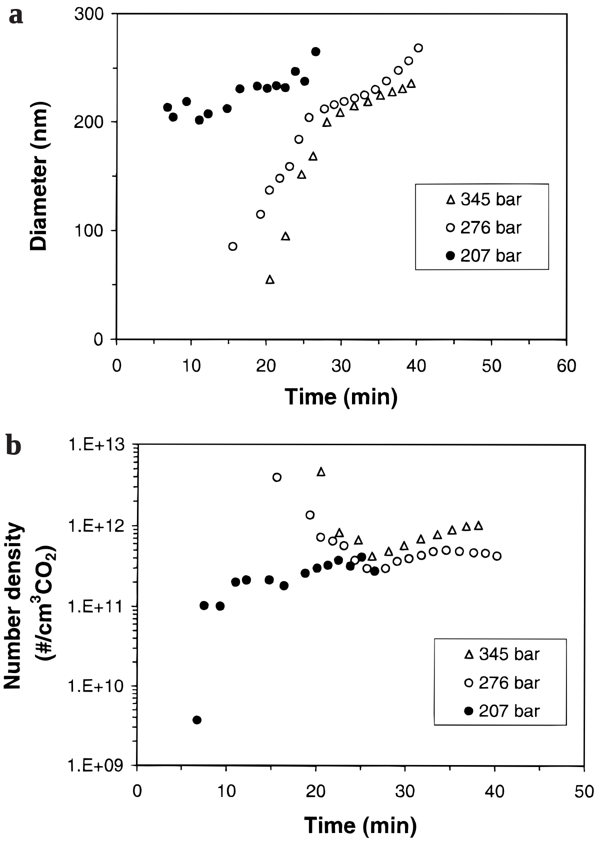

Figure 4. Dispersion polymerization of MMA in CO_2 at 65 °C with 20% MMA and 3% PDMS-*b*-P(MMA-*co*-MA) at various pressures: (a) average particle size and (b) particle number density.

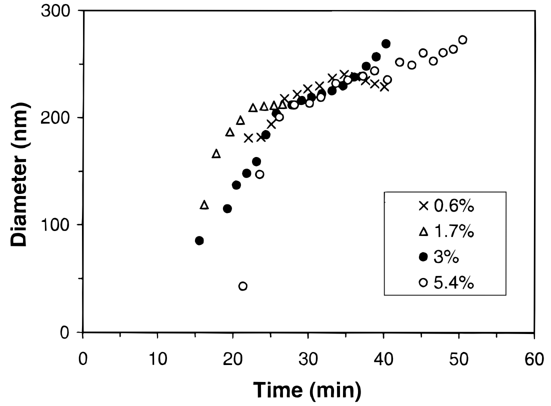

Figure 5. Average particle size in the dispersion polymerization of MMA in CO_2 at 65 °C and 276 bar with 20% MMA and various PDMS-*b*-P(MMA-*co*-MA) concentrations.

merizations stabilized by 5% PDMS-*b*-P(MMA-MA)/MMA (w/w). As the monomer concentration was increased from 10 to 20%, a modest decrease in the particle size and little change in the number density were observed (Figure 6a,b).

Since PMMA is soluble in its own monomer, MMA acts as a cosolvent in CO_2. As the MMA concentration increases, precipitation of growing PMMA chains is delayed. The adsorption of the stabilizer may decrease, although the concentration of stabilizer is more than adequate for high adsorption, given the results of the previous section. An increase in the solvent strength due to monomer will significantly increase PDMS chain extension from the particle surface enhancing steric stabilization.[35] In our case, the particle size decreases with monomer concentration since the stabilization of the PDMS chains increases. However, the final particle size increased with increasing monomer concentration as has been observed in other studies.[2,7,8,26,45] According to Paine's model,[11] the final particle size depends on the monomer concentration to the $^2/_3$ power due to polymerization kinetics, if the stabilization is constant.

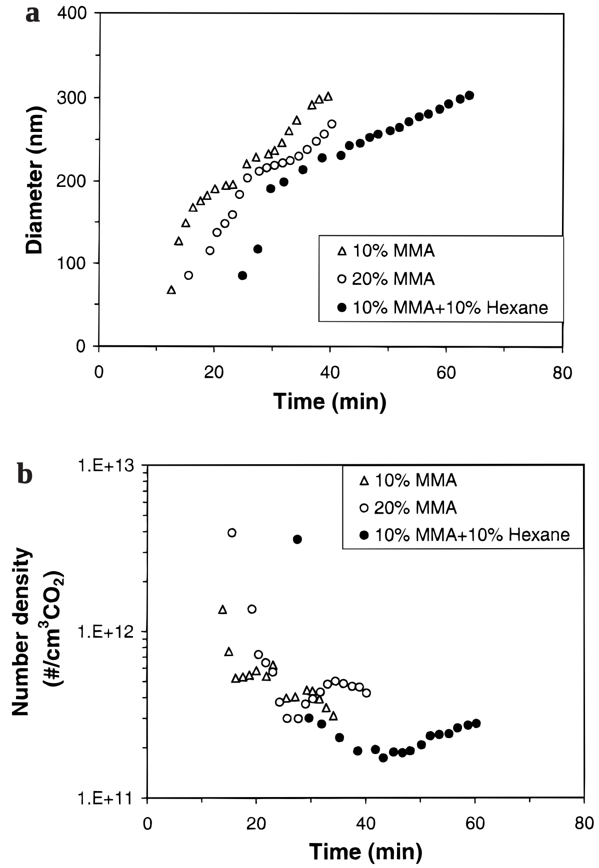

Figure 6. Dispersion polymerization of MMA in CO_2 at 65 °C and 276 bar with 3% PDMS-*b*-P(MMA-*co*-MA) at various monomer concentrations in CO_2: (a) average particle size and (b) particle number density.

To further study solvation of PDMS stabilizers, experiments were performed with 5% MMA/CO_2. The diameters reached 2 μm during the particle formation stage (not shown), indicating the extension of the short PDMS chains from the surface was insufficient to restrict coagulation, despite adequate stabilizer adsorption.

To improve the solvent quality, 10% hexane, a good solvent for PDMS, was added to the reaction mixture. The cosolvent raises the solvent refractive index and thus weakens the interparticle attractive van der Waals forces.[35] The improvement in the solvent quality for PDMS produces more extended tails and weaker interparticle interactions between tail segments. As shown in Figure 6a,b, the addition of hexane results in smaller particles with no significant change in particle number density. In the particle formation regime, either increasing the monomer concentration or adding organic cosolvent will enhance the PDMS chain extension and result in smaller particles.

Conclusions

The effect of stabilizers on the particle formation stage in dispersion polymerization of methyl methacrylate in supercritical CO_2 may be monitored successfully by in-situ turbidimetry. The block copolymer stabilizers produce 250 nm particles in the particle formation stage, whereas the particles are modestly larger for PFPE-COOH and much larger for the PDMS-mMA macromonomer. The ability to stabilize particles with PDMS as effectively as with PFOA during particle formation may be attributed to the large concentration of monomer, which acts as a cosolvent. The final particle number density remains constant to complete conversion for the PDMS-based stabilizer but increases for PFOA-*b*-PS due to formation and growth of new particles in block copolymer micelles. The less successful stabilization for PDMS-mMA indicates insufficient surface coverage since the PDMS segment is capable of providing strong stabilization on the basis of the results for PDMS-*b*-P(MMA-*co*-MA).

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