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# Communications to the Editor

## Dispersion Polymerization of 1-Vinyl-2-pyrrolidone in Supercritical Carbon Dioxide

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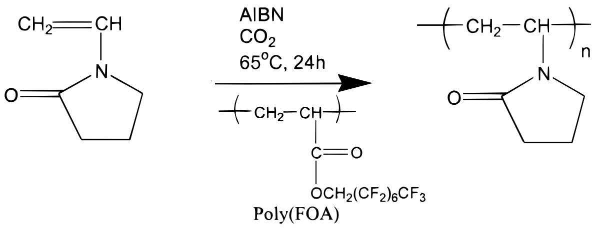
In recent years, carbon dioxide has proven to be an attractive solvent for the homogeneous polymerization of fluorinated monomers and heterogeneous processes such as dispersion polymerizations.[1−3] It has an easily accessible critical point with a $T_c$ of 31.1 °C and a $P_c$ of 73.8 bar.[4] Within this region, supercritical $CO_2$ exists as a low-viscosity medium with a tunable density. Carbon dioxide is also inert to free radicals which alleviates chain transfer reactions to solvent. Two classes of polymers have shown appreciable solubility in supercritical $CO_2$: amorphous fluoropolymers and silicones.[5] Both classes of materials have been found to be efficient stabilizers in the dispersion polymerization of olefinic monomers in carbon dioxide. In 1994, we reported the dispersion polymerization of methyl methacrylate (MMA) in supercritical carbon dioxide using a fluorinated polymeric surfactant, poly(1,1-dihydroperfluorooctyl acrylate) [poly(FOA)].[3] These polymerizations yielded micrometer-sized particles with narrow size distributions. After further investigation, this system was extended to include poly(dimethylsiloxane) [PDMS] which contained a polymerizable end group.[6] We have also successfully carried out the dispersion polymerization of styrene in carbon dioxide.[7,8] Initially, we reported that poly(FOA) was an ineffective stabilizer for this system, but more recent work has demonstrated its efficiency.[9] In this study higher pressures of $CO_2$ were employed which resulted in stable polymer colloids. The polymerizations produced relatively uniform and spherical particles (2.9−9.6 μm) and high yields. Diblock copolymers of poly(styrene) [PS] and poly(FOA) or PDMS have also been employed.

**Scheme 1. Polymerization of 1-Vinyl-2-pyrrolidone in $scCO_2$**



Limited research efforts have been reported on the dispersion polymerization of water-soluble vinylic monomers in carbon dioxide. Adamsky and Beckman reported the inverse emulsion polymerization of acrylamide in supercritical $CO_2$, but the dispersion process remains to be explored.[10] Herein we report the dispersion polymerization of 1-vinyl-2-pyrrolidone (VP) using low molecular weight poly(FOA) as the stabilizer. The effects of stabilizer concentration, monomer concentration, and $CO_2$ pressure on the resulting PVP colloid have been investigated. In addition, an extraction study has been conducted which suggests grafting of poly(FOA) on the PVP particles.

The synthetic procedure used to conduct the polymerizations is shown in Scheme 1. Initially, a 10 mL high-pressure reactor view cell was charged with the initiator [2,2′-azobis(isobutyronitrile)] and surfactant, and the system was purged with argon for 15 min. Degassed monomer was added to the cell via a syringe under an argon atmosphere. The cell was then pressurized with

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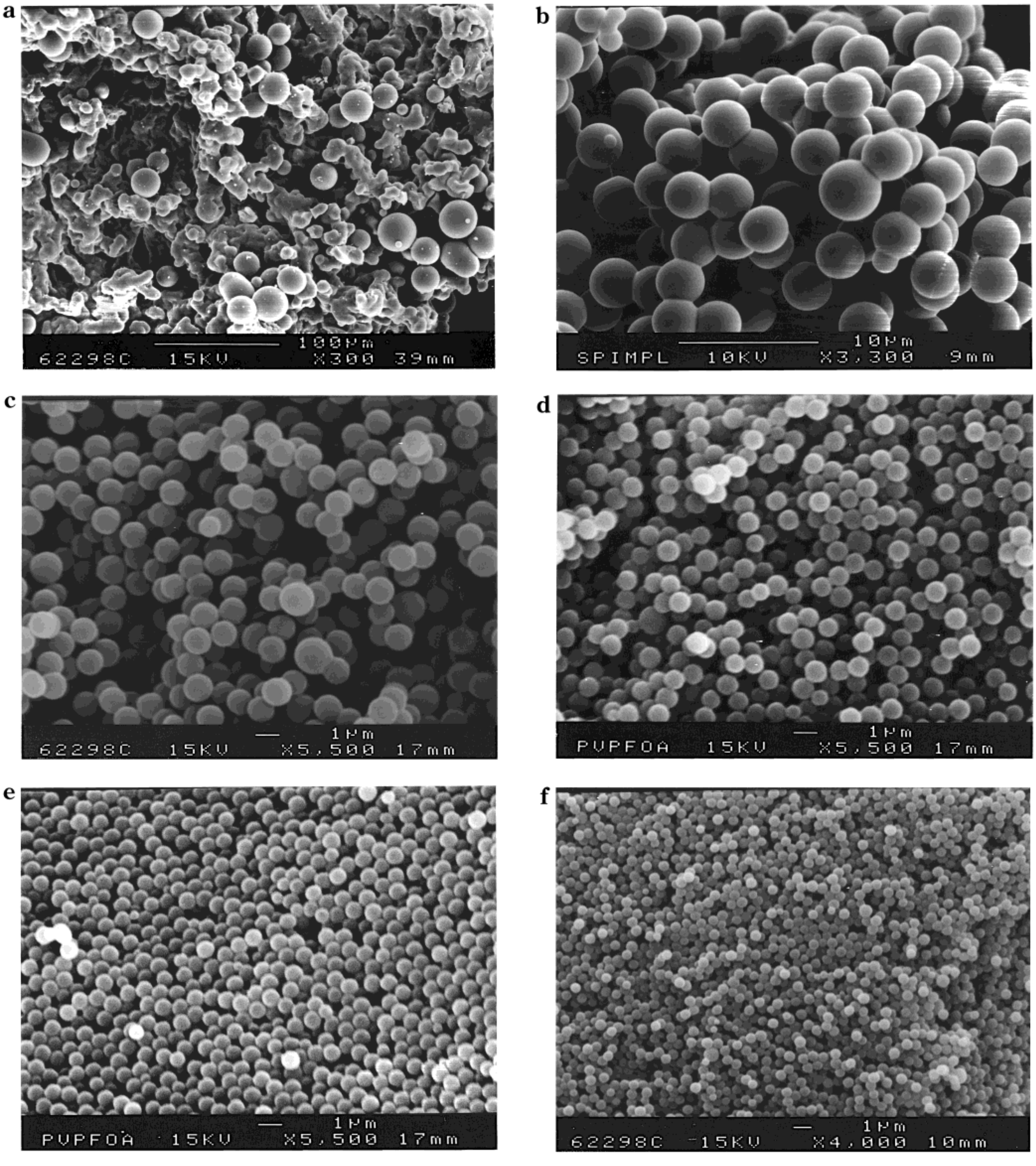

**Figure 1.** SEMs of PVP particles synthesized with various amounts of poly(FOA): (a) 0, (b) 0.25, (c) 0.5, (d) 2, (e) 4, and (f) 6 w/v %.

$CO_2$ to ~124 bar using an Isco syringe pump. The cell was heated to 65 °C, followed by the final pressurization to 340 bar. Initially, a clear solution was produced, but as the polymerization proceeded, the $CO_2$ phase became hazy and eventually developed into a milky polymer colloid. The reaction was allowed to proceed for 24 h with magnetic stirring and was monitored by visual observation through the sapphire windows on the cell. At the end of the reaction, the cell was cooled to room temperature, and the $CO_2$ was slowly vented from the cell.

The low molecular weight poly(FOA) (Scheme 1) surfactant used in this study was prepared by a solution free-radical polymerization in supercritical $CO_2$ as previously described.[11] Cloud point experiments indicate that poly(FOA) is soluble in pure $CO_2$ at the polymerization conditions.[12]

Liquid and supercritical $CO_2$ have a low dielectric constant. However, some polar molecules such as methanol are solubilized in $CO_2$ because of their vapor pressure. Other polar molecules such as water, amides, ureas, urethanes, and azo dyes show relatively poor

**Table 1. Pressure Study for 1-Vinyl-2-pyrrolidone Polymerization in $CO_2$[a]**

| entry | initial pressure, bar | final pressure, bar | $\Delta P^b$ (bar) | yield, % | Dn,[c] $\mu$m | PSD[d] | latex stability[e] |
|---|---|---|---|---|---|---|---|
| 7 | 351 | 337 | −14 | 82 | 1.00 | 1.10 | stable |
| 8 | 282 | 310 | +28 | 77 | 1.20 | 1.16 | stable |
| 9 | 220 | 268 | +48 | 63 | 1.29 | 1.10 | stable |
| 10 | 141 | 155 | +14 | 64 | 1.20 | 1.18 | ppt |

[a] Reaction conditions: 0.0200 g of AIBN; 2.0 g of VP; 2 w/v % poly(FOA); $T = 65$ °C; 3 h reaction time. [b] $\Delta P$ = change in pressure. [c] Dn = mean particle diameter. [d] PSD = particle size distribution. [e] ppt = precipitate formation.

solubility in $CO_2$.[13] VP is miscible with carbon dioxide at the conditions the polymerizations were conducted, displaying clear solutions at the beginning of the reaction. In the absence of stabilizer, the solution developed a milky, white, opaque appearance after 3 h, and precipitate formation was observed after 5−6 h. Scanning electron microscopy (SEM) was used to determine the morphology of the PVP, and as expected, the polymer displayed a nondescript morphology (Figure 1a). The polymerizations conducted in the presence of surfactant produced free-flowing powders after venting the $CO_2$. SEM revealed that the polymers consisted of micrometer-sized spheres with relatively narrow size distributions. As the surfactant concentration increased from 0.25 to 6 w/v %, the average particle size decreased. These results are in agreement with the findings of Dawkins et al., who observed that the particle size of the final latex decreases with increasing concentration of the stabilizer.[14] Additionally, O'Neill et al. observed smaller particle sizes with increasing stabilizer concentration in the dispersion polymerization of MMA in $scCO_2$, whereby the mechanism of particle formation was examined.[15] The particle size dependence on surfactant concentration can be explained in terms of the surface area of the polymer particles. An increase in surfactant concentration enables more surface area stabilization. It has also been observed that broader particle size distributions of a latex result with increasing stabilizer concentration. However, the particle size distributions remained fairly constant in this study with the exception of the polymer spheres produced from the reaction ran with 0.25 w/v % poly(FOA). This slightly broader distribution can be explained in terms of the polymer colloid stability. When no poly(FOA) surfactant was added to the polymerization, low conversion and precipitation resulted after 5−6 h. When 0.25 and 0.5 w/v % poly(FOA) surfactant were used, precipitation occurred after 9 and 18 h, respectively, with higher conversions. The remaining reactions at higher surfactant concentrations did not produce any visible precipitate but remained stable throughout the entire reaction period.

Static light scattering techniques were used to obtain molecular weight information for PVP where 2 w/v % poly(FOA) was employed. It appears that very high molecular weight polymer is produced [$M_w = 3.06 \times 10^6$ g/mol]. An initial attempt to use gel permeation chromatography ($CH_2Cl_2$) for molecular weight data resulted in polymer samples eluting the column before the highest molecular weight standard [$M_w = 1 \times 10^6$ g/mol]. Future work will focus on using other methods, such as intrinsic viscosity techniques, to confirm this result.

Two mechanisms have been proposed for nonionic stabilization: steric and depletion stabilization.[16] For the steric stabilization mechanism, modes of anchoring include adsorption, absorption, and grafting.[17] Although it is difficult to distinguish between the various modes,

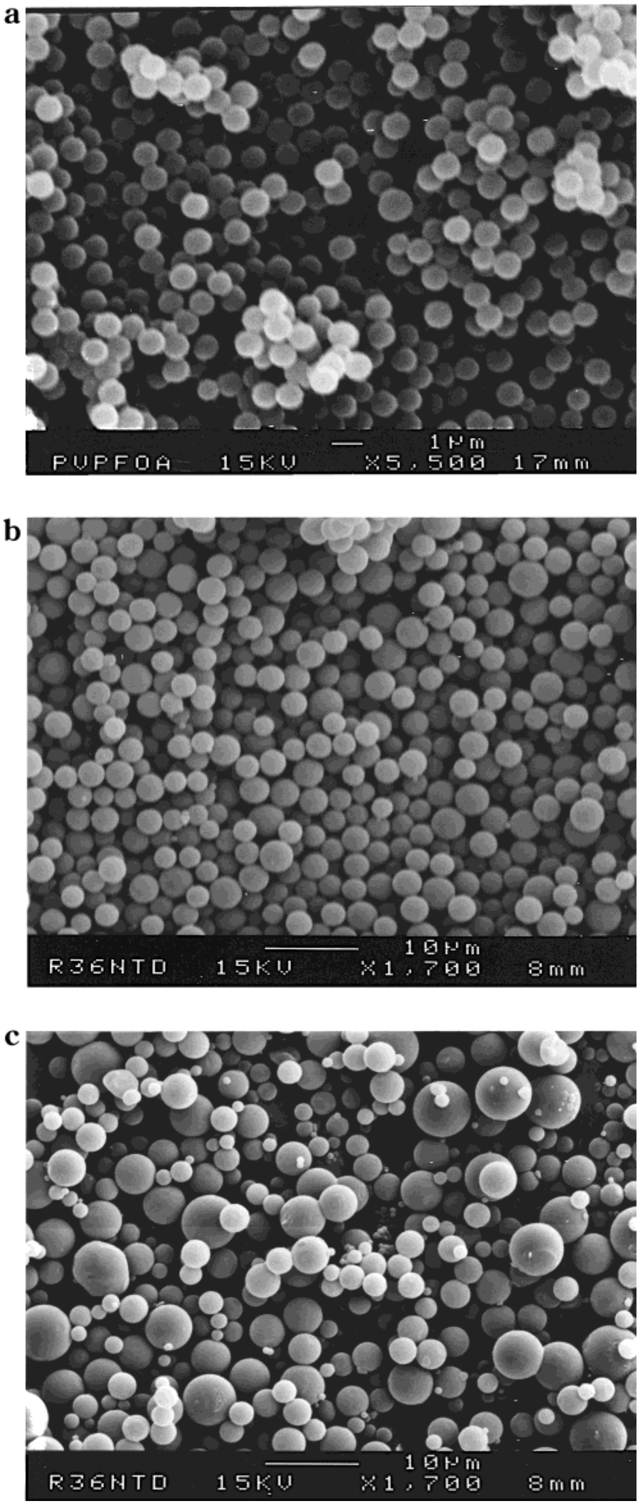

**Figure 2.** SEMs of PVP particles synthesized with (a) 20, (b) 40, and (c) 60 w/v % VP.

it appears that poly(FOA) becomes chemically grafted onto the PVP particles. An extraction study was conducted whereby an amount of PVP was placed in a Soxhlet extractor with methanol for 24 h, allowing the PVP homopolymer to fully dissolve.[18] After this time, a precipitate remained in the Soxhlet thimble and was isolated and dried under vacuum. Since poly(FOA) is insoluble in methanol, it was assumed that the precipitate was residual stabilizer. However, in examining the solubility properties of this material, it would not fully dissolve in Freon-113, a good solvent for poly(FOA). Even after Soxhlet extraction in Freon-113 for 24 h, the precipitate remained. An attempt was made to dissolve the material in a mixture of methanol and Freon-113, but by visual observation, the polymer only swelled to twice its original size. FTIR characterization confirmed the existence of both polymers in this material which suggests graft copolymerization with poly(FOA) and PVP. The mechanism by which grafting occurs is not completely understood but may take place through chain transfer reactions with the poly(FOA) backbone.

The effect of different pressures on the PVP colloid was investigated as shown in Table 1. The solvency of the $CO_2$ medium can be altered through small changes in temperature and pressure. The density of $CO_2$ increases from ca. 0.60 to 0.85 g/mL as the pressure changes from 141 to 351 bar at 65 °C.[19] Moderate yields were achieved in all cases with narrow particle size distributions. Additionally, all reactions produced stable latexes with the exception of the lowest pressure, which resulted in visibly flocculated product after 20 min.

The pressure profile during the course of each polymerization was similar to that observed by us for other monomer systems. The reaction conducted at 351 bar resulted in a pressure decrease by 14 bar, while the remaining reactions experienced increases in pressure. This pressure increase has been observed with other systems such as MMA and styrene. Since most monomers have a negative reaction volume, conversion of monomer to polymer should result in a pressure decrease for a homogeneous solution polymerization. However, pressure increases may result if $CO_2$ is not sufficiently solubilized in the particle phase. Further investigations into the swelling behavior of PVP in $CO_2$ will hopefully account for these complex pressure changes.

The effect of the initial concentration of the monomer was also investigated, and the SEM micorgraphs can be found in Figure 2. These results show that as monomer concentration increases, the average particle size and particle size distribution increase. Antl et al. suggested that the particle formation process is related to the solvency of the dispersion medium.[20] Since PVP is soluble in its monomer, a VP-rich phase increases the critical degree of polymerization at which PVP oligomeric radicals phase separate. The time scale for stable nuclei formation is lengthened. Additionally, the adsorption efficiency of the surfactant decreases, leading to fewer nuclei and larger particles. While the 20 w/v % VP reaction produced a stable latex during the entire reaction period, the 40 and 60 w/v % VP collapsed after 2.5 and 1.5 h, respectively. With high VP concentrations, the $CO_2$ medium becomes a more polar environment, decreasing the solubility of poly(FOA) which affects latex stability.

In conclusion, low molecular weight poly(FOA) has been used in the dispersion polymerization of VP in supercritical $CO_2$. Increasing concentrations of poly(FOA) yielded a decrease in particle diameter, while increasing the monomer concentration produced an increase in particle size. No significant change was observed in the particle morphology for polymerizations conducted at different pressures. We are currently investigating the swelling behavior of PVP in $CO_2$, and viscosity measurements for molecular weight determination are under way. Studies to confirm whether graft copolymerization occurs are also under way.

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