Polymerization of Vinylpyrrolidone in Supercritical Carbon Dioxide with a Diblock Copolymer Stabilizer

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Introduction. Replacement of harmful organic solvents used in polymer chemistry represents a key topic within industry, for economic and environmental reasons. Supercritical carbon dioxide is an attractive candidate as its moderate critical parameters of $T_c = 304$ K and $p_c = 7.4$ MPa are easily accessible, and a “fine-tuning” of the solvent quality is possible by the variation of pressure and/or temperature.[1] Therefore, research has highlighted that sc-CO_2 is applicable in many aspects of polymer chemistry.[2−6]

The solubility of most commonly used polymers in supercritical CO_2 is significantly molecular weight dependent. Thus, precipitation polymerizations are often observed. Recent work has introduced the use of stabilizers, which prevent aggregation and precipitation during polymerization in sc-CO_2.[7] Although there are various types of stabilizers, they generally consist of a “CO_2-philic” and a “CO_2-phobic” subunit.[8] It has been demonstrated that a poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS) copolymer can act as a suitable stabilizer in the free radical dispersion polymerization of styrene in sc-CO_2.[2]

We have now focused on related diblock copolymer stabilizers in the synthesis of poly(vinylpyrrolidone) (PVP).[9] The synthesis of the water-soluble PVP in sc-CO_2 is of special significance, since conventional dispersion and emulsion polymerizations in aqueous reaction systems are impossible. In our polymerizations in sc-CO_2, easily accessible and well-characterized PS-*b*-PDMS copolymers should act as a surfactant and stabilize the growing PVP particles. The concentration of the stabilizer has been varied to study the influence on the morphology of the obtained PVP particles.

Experimental Section. a. Materials. Carbon dioxide (Linde, grade 4.5) was dried over molecular sieves (4 Å), before use. The monomer vinylpyrrolidone (VP), from Aldrich (99+%), was deinhibited by using an activated basic alumina column. The initiator, 2,2′-azobis(isobutyronitrile) (AIBN, Fluka), was recrystallized from methanol and vacuum-dried before use.

b. Diblock Copolymer. Poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS) diblock copolymers were synthesized by living anionic polymerization according to literature procedures.[10] The copolymers were dried under vacuum at 313 K. Molecular weights and polydipersities were determined by gel permeation chromatography (GPC) for the PS intermediate. After diblock formation, the ratio polystyrene/poly(dimethylsiloxane) was determined by nuclear magnetic resonance (^{1}H NMR). The characteristics of the diblock copolymer selected for this study are $M_n(\text{PS}) = 6100$, $M_w/M_n(\text{PS}) = 1.09$, $M_n(\text{PDMS}) = 19\,500$, $M_n(\text{diblock copolymer}) = 25\,600$, and $M_w/M_n(\text{diblock copolymer}) = 1.05$.

c. Polymerizations in Carbon Dioxide. The polymerizations were conducted in a 60 mL stirred autoclave (Medimex, 1.4980 steel alloy). Typically 4 g of monomer, 50 mg of AIBN, and the desired amount of stabilizer were added to the autoclave. The mixture was degassed three times by freezing, applying vacuum and flushing with carbon dioxide.

For polymerization, the reaction mixture was stirred and compressed; CO_2 was added by a HPLC pump (Jasco, HP 880) to ∼70 bar. Then the autoclave was heated to 353 K; CO_2 was slowly added to the system until the desired temperature and pressure were reached, which were held for 8 h. After polymerization, the autoclave was cooled to room temperature (<5 K/min), whereupon the pressure was reduced (<2 bar/min) and the polymer was recovered. The particles were characterized without further posttreatment.

d. Characterization. Molecular weight data for the PVP samples were obtained with a Waters 590 gel permeation chromatograph with a styrene−divinylbenzene (SDV) column of the dimensions 500 mm × 8 mm, particle size 10 μm, and pore sizes of 500, 10^5, and 10^6 Å. The solvent used was water at 20 °C; the eluted polymer was detected by a UV-Soma /RI-ERC system. Molecular weights were calculated using narrowly distributed poly(ethylene oxide) (PEO) standards. SEM characterization was achieved with a LEO EM912 scanning electron microscope (1 kV, InLens). NMR measurements were obtained with a Bruker 300 MHz instrument.

Results and Discussion. The polymerization of vinylpyrrolidone without any stabilizer results in a white or slightly yellow, hard and glassy material. Because of the high glass transition temperature of PVP between 140 and 175 °C, dependent on the amount of remaining solvents, PVP is thermally not easy to process. PVP is soluble in water, alcohol, and other polar solvents as reported elsewhere.[11] A scanning electron microscope (SEM) picture of such a sample obtained without additional stabilizer is shown in Figure 1.

To obtain a more processable PVP, we started our experiments with PS-*b*-PDMS stabilizers. The addition of a low percentage of a diblock stabilizer to the polymerization mixture results in a powdery PVP material which can be easily recovered from the reaction vessel. An electron micrograph of this PVP sample is shown in Figure 2; the sample was generated by the procedure described in detail in the Experimental Section using 1.1 wt % of the PS-*b*-PDMS diblock copolymer. Uniform particles with a narrow size distribution (approximately 1 μm diameter) were obtained which are slightly agglomerated like “glued” spheres. This slight agglomeration is probably caused by a plasticization of the particle shells under the polymerization conditions. The core of the particles appear to be unplasticized. In contrast to PVP, the initiator AIBN and the monomer show reasonable solubility in sc-CO_2. A partial deaggregation of the product occurs under mechanical stress or by redispersing the particles in a nonsolvent for PVP. Figure 3 displays an atomic force micrograph (AFM) of the PVP particles obtained after redispersion in *n*-heptane and drop-casting onto a glass substrate. The deaggregation effect indicates a soft shell

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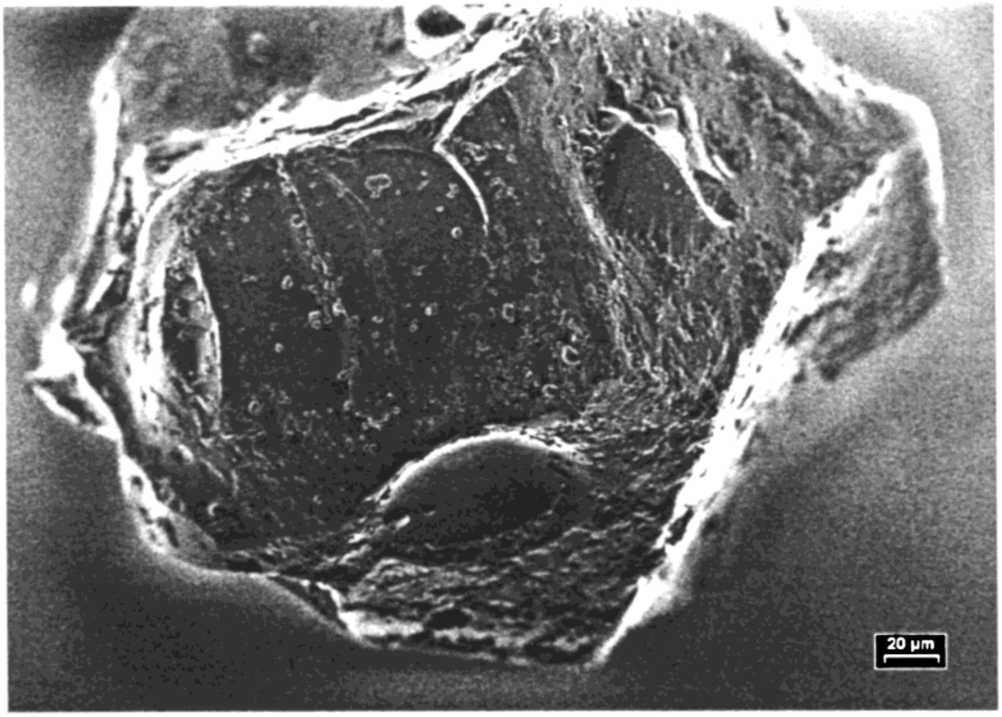

Figure 1. Scanning electron micrograph of PVP synthesized in sc-CO_2 without stabilizer (80 °C, 390 bar, 8 h).

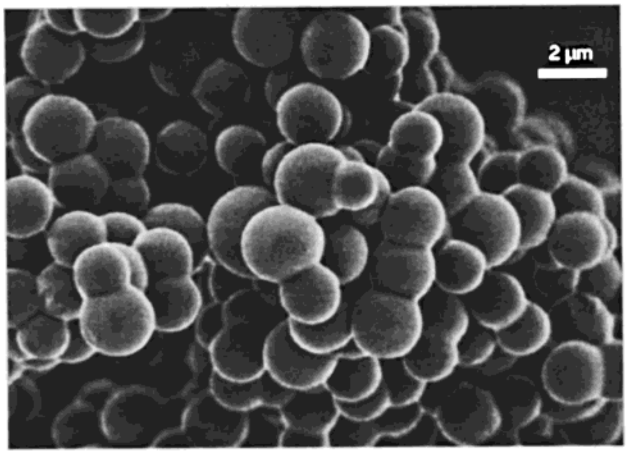

Figure 2. Scanning electron micrograph of PVP particles synthesized with 1.1 wt % PS-*b*-PDMS diblock stabilizer in sc-CO_2 (80 °C, 390 bar, 8 h).

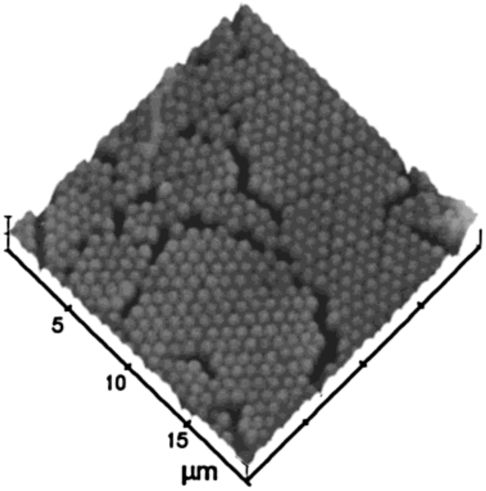

Figure 3. Atomic force micrograph of PVP particles synthesized with 1.1 wt % diblock stabilizer in sc-CO_2. The sample was redispersed in *n*-heptane and deposited on a glass substrate.

of the particles as a consequence of the incorporation of "soft" stabilizer molecules (T_g of PDMS is approximately −120 °C at ambient pressure).

In a next step, the concentration of the diblock stabilizer has been varied between 1 and 5 wt %; the resulting polymers have been analyzed by GPC and scanning electron microscopy (Table 1). With increasing concentration of stabilizer the particles become increasingly aggregated; the particles are larger and lose their uniform spherical shape. We interpret this unusual finding by an increasing amount of incorporated, "soft" stabilizer molecules. They are located in the outer sphere of the particles, which leads to a plasticized shell and allows the particles to fuse and to form larger aggregates. Therefore, a target of further investigations will be an in-situ study of the growing polymer particles at stabilizer concentrations between 1 and 5 wt %, e.g., by means of turbidimetric investigations.

Table 1. GPC Results and Morphology of the PVP-Samples Synthesized with Different Amounts of the Diblock Stabilizer

sample	concn of diblock stabilizer, wt %	M_w (GPC)[a]	M_w/M_n	morphology
PVP1	0	190 000	9.8	glassy material irregular shape, $d \gg 1$ µm
PVP2	1.1	240 000	9.7	uniform microspheres, narrow size distribution, $d \approx 1$ µm
PVP3	1.9	240 000	>10	aggregated spheres, broad size distribution, $d > 1$ µm
PVP4	5.1	253 000	9.7	aggregated spheres, broad size distribution, $d \gg 1$ µm

[a] Water, PEO calibration.

The molecular weights close to $M_w = 240\,000$ g/mol of all PVP samples synthesized in sc-CO_2 are high compared to PVP obtained under conventional reaction conditions.[11] This effect is often found in dispersion polymerizations. However, our samples are characterized by an unusual high polydispersity M_w/M_n probably due to the inhomogeneous, nonstationary reaction conditions and/or a high radical transfer rate to the monomer.[12] For all samples, the conversion of the monomer to PVP was estimated to be quantitative.

Conclusion. The radical polymerization of vinylpyrrolidone in sc-CO_2 was carried out in the presence of a poly(styrene-*b*-dimethylsiloxane) diblock copolymer, which acts as an effective stabilizer. In contrast to the polymerization without stabilizer, the use of our PS-*b*-PDMS stabilizer leads to the formation of uniform microparticles of a regular spherical shape. This dispersion polymerization of vinylpyrrolidone in sc-CO_2 was found to be very sensitive to the reaction parameters, especially the concentration of stabilizer. The broad molecular weight distribution of the products differs from a conventional dispersion polymerization of the vinylpyrrolidone monomer. This fact can be interpreted by a surface plasticization of the growing particles leading to inhomogeneous polymerization conditions.

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